## The Iron and Steel Institute

# Second Report

ON

# REFRACTORY MATERIALS

BEING A REPORT BY

THE JOINT REFRACTORIES RESEARCH COMMITTEE OF
THE IRON AND STEEL INDUSTRIAL RESEARCH COUNCIL

AND

THE BRITISH REFRACTORIES RESEARCH ASSOCIATION

*Special Report No.* 1. First Report of the Corrosion Committee. Price 16/-. (Members, 10/-.)

*Special Report No.* 2. Fourth Report on the Heterogeneity of Steel Ingots. Price 16/-. (Members, 10/-.)

*Special Report No.* 3. First Report of the Steel Castings Research Committee. Price 10/-. (Members, 5/-.)

*Special Report No.* 4. Fifth Report on the Heterogeneity of Steel Ingots. Price 10/-. (Members, 5/-.)

*Special Report No.* 5. Second Report of the Corrosion Committee. Price 16/-. (Members, 10/-.)

*Special Report No.* 6. First Report of the Blast-Furnace Practice Sub-Committee. Price 10/-. (Members, 5/-.)

*Special Report No.* 7. Blast-Furnace Linings. Price 10/-. (Members, 5/-.)

*Special Report No.* 8. Third Report of the Corrosion Committee. Price 16/-. (Members, 10/-.)

*Special Report No.* 9. Sixth Report on the Heterogeneity of Steel Ingots. Price 16/-. (Members, 10/-.)

*Special Report No.* 10. Waste-Heat Boilers in Open-Hearth Practice. (Second Report of the Open-Hearth Committee.) Price 10/-. (Members, 5/-.)

*Special Report No.* 11. The Work of the Corrosion Committee. By Dr. W. H. Hatfield, F.R.S. Issued free on application.

*Special Report No.* 12. The Work of the Heterogeneity of Steel Ingots Committee. By Dr. W. H. Hatfield, F.R.S. Issued free on application.

*Special Report No.* 13. Fourth Report of the Corrosion Committee. Price 16/-. (Members, 10/-.)

*Special Report No.* 14. First Report of the Alloy Steels Research Committee. Price 16/-. (Members, 10/-.)

*Special Report No.* 15. Second Report of the Steel Castings Research Committee. Price 10/-. (Members, 5/-.)

*Special Report No.* 16. Seventh Report on the Heterogeneity of Steel Ingots. Price 16/-. (Members, 10/-.)

*Special Report No.* 17. The Work of the Coke Research Committees of the Iron and Steel Industrial Research Council. Price 10/-. (Members, 5/-.)

*Special Report No.* 18. Reports upon Blast-Furnace Field Tests. I.—An Investigation of a Blast-Furnace Smelting principally Lincolnshire Ores at the Frodingham Works of the Appleby-Frodingham Steel Co., Ltd. Price 10/-. (Members, 5/-.)

NOTE.—The First, Second and Third Reports of the Committee on the Heterogeneity of Steel Ingots were originally printed in the *Journal of the Iron and Steel Institute* as follows:

First Report: 1926, No. I., pp. 39–151.
Second Report: 1928, No. I., pp. 401–547.  Price 16/-.  (Members, 10/-.)
Third Report: 1929, No. I., pp. 305–376.  Price 10/-.  (Members, 5/-.)

Reprints of the Second and Third Reports are still available, but the First Report is out of print.

# CONTENTS.

## SECTION A.  FOREWORD.

## SECTION B.  STEELWORKS REFRACTORIES.

## SECTION C.  BLAST-FURNACE REFRACTORIES.

## SECTION  D.

## PLATES.

NOTE.—The First, Second and Third Reports of the (
the Heterogeneity of Steel Ingots were originally printed i
*of the Iron and Steel Institute* as follows:

First Report: 1926, No. I., pp. 39–151.
Second Report: 1928, No. I., pp. 401–547.  Price 16/-. (Members, 10/-.)
Third Report: 1929, No. I., pp. 305–376.  Price 10/-. (Members, 5/-.)

Reprints of the Second and Third Reports are still available, but the First Report is out of print.

# CONTENTS.

## SECTION A.  FOREWORD.

## SECTION B.  STEELWORKS REFRACTORIES.

## SECTION C.  BLAST-FURNACE REFRACTORIES.

## SECTION  D.

## PLATES.

# Section A.   Foreword.

## Foreword.

Since the issue of the First Report on Refractory Materials *
by the Joint Refractories Research Committee of the Iron and Steel
Industrial Research Council and the British Refractories Research
Association in March, 1939, a very considerable amount of work
has been carried out on the various types of refractory used in the
iron and steel industry and published in the confidential bulletins
of the B.R.R.A.   It has therefore appeared desirable to reprint
certain of these papers as a Second Report.   It was further decided
to include a summary of other recent investigations in this report.

For some time prior to the outbreak of war, the Open-Hearth
Refractories Joint Panel had devoted its attention chiefly to basic
refractories.   The interest was such that when hostilities began,
the B.R.R.A. re-arranged a part of its programme with a view to
preparing a bulletin devoted to this subject.   This bulletin, pub-
lished in September, 1940, contained a comprehensive review on
basic refractory materials and eleven papers describing the results
of original research.   In view of the difficulty in obtaining supplies
of magnesite in war time, it was inevitable that a major proportion
of these research papers should deal with alternative types of basic
refractory, particularly stabilised dolomite.   This work has con-
tinued during 1941, and it is felt that, as a result, a better apprecia-
tion of the constitution and behaviour of basic refractories has been
attained.   Certain of the papers on stabilised dolomite are reprinted
in this Second Report.

Supplementary to this research has been the preparation of a
report on " Methods of Testing Basic Refractory Raw Materials
and Products " ; this was published in July, 1940, and was cir-
culated within the steel industry by the British Iron and Steel
Federation.   It was felt, however, that the tests described should
be used as a preliminary to service tests ; the Open-Hearth Panel
therefore drew up a standard service test-sheet for basic refractories
used in the open-hearth furnace, and this was published in March,
1941.   The Panel has also sponsored observational work on the
conditions in an open-hearth furnace as they affect the life of the
roof.   The results of this study have been published by The Iron
and Steel Institute.

The Blast Furnace Refractories Panel has continued to meet,
and a detailed examination of the temperature gradients in the lining
of a blast furnace throughout a campaign has been made.   The

* *Iron and Steel Institute*, 1939, *Special Report No. 26.*

results of this work are reprinted in the present Report. Work has also been carried out for the Blast Furnace Refractories Panel on the production of carbon blocks.

In conclusion it may be stated that war conditions have stimulated research activity in the refractories industry ; this is exemplified by the recent formation of two sub-committees of the Open Hearth Refractories Panel which deal respectively with Basic Bricks and Casting-Pit Refractories. The co-operative spirit between manufacturer, user and research worker has been greatly developed.

T. SWINDEN (*Chairman, Joint Refractories Research Committee*).

A. T. GREEN (*Director of Research B.R.R.A.*).

## CONSTITUTION OF COMMITTEES AND PANELS.

JOINT REFRACTORIES RESEARCH COMMITTEE OF THE IRON AND STEEL INDUSTRIAL RESEARCH COUNCIL (BRITISH IRON AND STEEL FEDERATION) AND THE BRITISH REFRACTORIES RESEARCH ASSOCIATION.

| | |
|---|---|
| Dr. T. SWINDEN (*Chairman*) | The United Steel Companies, Ltd. |
| Mr. E. C. EVANS . | British Iron and Steel Federation. |
| Mr. G. H. JOHNSON . . | Kettering Iron and Coal Co., Ltd. |
| Mr. R. P. SMITH . . | The United Steel Companies, Ltd. |
| Col. A. STEIN . . . | Messrs. John G. Stein and Co., Ltd. |
| Lt.-Col. C. W. THOMAS, T.D. | Messrs. E. J. and J. Pearson, Ltd. |
| Mr. F. WEST . . . | Derbyshire Silica Firebrick Co., Ltd. |
| Mr. A. T. GREEN . . | British Refractories Research Association (Director of Research). |

OPEN-HEARTH REFRACTORIES JOINT PANEL OF THE IRON AND STEEL INDUSTRIAL RESEARCH COUNCIL (BRITISH IRON AND STEEL FEDERATION) AND THE BRITISH REFRACTORIES RESEARCH ASSOCIATION.

| | |
|---|---|
| Dr. T. SWINDEN (*Chairman*) | The United Steel Companies, Ltd. |
| Mr. J. R. ADDERLEY . | Messrs. E. J. and J. Pearson, Ltd. |
| Dr. J. H. CHESTERS . | The United Steel Companies, Ltd. |
| Mr. E. J. CRAWLEY . | General Refractories, Ltd. (Sheffield). |
| Dr. A. H. B. CROSS | Brown-Firth Research Laboratories. |

| | |
|---|---|
| Mr. M. Douglas . . | Refractory Brick Company of England, Ltd. |
| Dr. J. M. Ferguson . | Messrs. Colvilles, Ltd. |
| Mr. C. S. Graham . | Messrs. John Lysaght, Ltd. |
| Mr. N. Gray . . | Messrs. Guest Keen Baldwins Iron and Steel Co., Ltd. |
| Mr. J. Holland . | Messrs. Pickford Holland and Co., Ltd. |
| Mr. J. F. Hyslop . | Messrs. John G. Stein and Co., Ltd. |
| Mr. T. R. Lynam . | Oughtibridge Silica Firebrick Co., Ltd. |
| Mr. A. McKendrick . | General Refractories, Ltd. (Glasgow). |
| Dr. D. F. Marshall . | Park Gate Iron and Steel Co., Ltd. |
| Mr. W. Boyd Mitchell | Messrs. James Dougall and Sons, Ltd. |
| Mr. D. C. Muir . . | Consett Iron Co., Ltd. |
| Mr. H. Oliver . . | Derbyshire Silica Firebrick Co., Ltd. |
| Dr. J. R. Rait . . | Messrs. Wm. Jessop and Sons, Ltd. |
| Dr. W. J. Rees . . | Department of Refractory Materials, The University, Sheffield. |
| Dr. R. J. Sarjant . | Messrs. Hadfields, Ltd. |
| Mr. J. Sinclair-Kerr . | Lancashire Steel Corporation, Ltd. |
| Dr. A. E. J. Vickers . | Imperial Chemical Industries, Ltd. |
| Mr. A. T. Green . | British Refractories Research Association. |
| Mr. A. E. Dodd . . | British Refractories Research Association. |

## BASIC BRICKS SUB-COMMITTEE.

| | |
|---|---|
| Mr. A. T. Green (*Chairman*) | British Refractories Research Association. |
| Mr. A. A. Chadeyron . | Cleveland Magnesite and Refractory Co., Ltd. |
| Dr. J. H. Chesters | The United Steel Companies, Ltd. |
| Mr. E. J. Crawley | General Refractories, Ltd. (Sheffield). |
| Mr. J. Holland . | Messrs. Pickford Holland and Co., Ltd. |
| Mr. W. Hugill . | British Refractories Research Association. |
| Mr. J. F. Hyslop | Messrs. John G. Stein and Co., Ltd. |
| Mr. T. R. Lynam | Oughtibridge Silica Firebrick Co., Ltd. |
| Mr. D. C. Muir . | Consett Iron Co., Ltd. |
| Dr. J. R. Rait . | Messrs. Wm. Jessop and Sons, Ltd. |

Dr. W. J. REES .     Department of Refractory Materials, The University, Sheffield.

Dr. G. R. RIGBY .     British Refractories Research Association.

Mr. A. E. DODD .     British Refractories Research Association.

CASTING-PIT REFRACTORIES SUB-COMMITTEE.

Mr. A. T. GREEN (*Chairman*),     British Refractories Research Association.

Mr. S. H. BROOKS . .     Messrs. J. and J. Dyson, Ltd.

Dr. J. H. CHESTERS . .     The United Steel Companies, Ltd.

Mr. A. MARSHALL . .     Messrs. Thos. Marshall and Co. (Loxley), Ltd.

Dr. D. F. MARSHALL . .     Park Gate Iron and Steel Co., Ltd.

Mr. A. McKENDRICK . .     General Refractories, Ltd. (Glasgow).

Dr. J. R. RAIT . . .     Messrs. Wm. Jessop and Sons, Ltd.

Dr. W. J. REES . . .     Department of Refractory Materials, The University, Sheffield.

Dr. G. R. RIGBY .     British Refractories Research Association.

Mr. J. F. TREVOR     Messrs. John Knowles and Co. (Wooden Box), Ltd.

Mr. B. WRAGG .     Messrs. Thos. Wragg and Sons (Sheffield), Ltd.

Mr. A. E. DODD .     British Refractories Research Association.

BLAST FURNACE REFRACTORIES JOINT PANEL OF THE IRON AND STEEL INDUSTRIAL RESEARCH COUNCIL (BRITISH IRON AND STEEL FEDERATION) AND THE BRITISH REFRACTORIES RESEARCH ASSOCIATION.

Mr. G. H. JOHNSON (*Chairman*),     Kettering Iron and Coal Co., Ltd.

Mr. P. A. ABERNETHY . .     Messrs. Colvilles, Ltd.

Mr. A. H. DODD . .     Messrs. Newton Chambers and Co., Ltd.

Mr. E. C. EVANS . .     British Iron and Steel Federation.

Mr. W. G. GIRLING . .     Messrs. H. Foster and Co., Ltd.

Mr. H. J. C. JOHNSTON .     Leeds Fireclay Co., Ltd.

Mr. R. McGREGOR . .     Appleby-Frodingham Steel Co., Ltd.

| | |
|---|---|
| Dr. W. J. REES . . . | Department of Refractory Materials, The University, Sheffield. |
| Mr. J. H. RIDSDALE . . | Messrs. Guest Keen Baldwins Iron and Steel Co. Ltd. |
| Mr. R. SHARP . . . | Stanton Ironworks Co., Ltd. |
| Col. A. STEIN . . . . | Messrs. John G. Stein and Co., Ltd. |
| Dr. T. SWINDEN . . . | The United Steel Companies, Ltd. |
| Lt.-Col. C. W. THOMAS, T.D. | Messrs. E. J. and J. Pearson, Ltd. |
| Mr. F. WEST . . . | Derbyshire Silica Firebrick Co., Ltd. |
| Mr. A. T. GREEN . . | British Refractories Research Association. |
| Dr. G. R. RIGBY . . | British Refractories Research Association. |
| Mr. J. M. RIDGION . | British Iron and Steel Federation. |

TESTING COMMITTEE OF THE B.R.R.A.

| | |
|---|---|
| Dr. R. J. SARJANT (*Chairman*) | Messrs. Hadfields, Ltd. |
| Mr. A. L. BRADLEY | Refractory Brick Company of England, Ltd. |
| Dr. J. H. CHESTERS | The United Steel Companies, Ltd. |
| Dr. A. H. B. CROSS | Brown-Firth Research Laboratories. |
| Mr. W. T. GARDNER | Messrs. Woodall-Duckham Co., Ltd. |
| Mr. J. F. HYSLOP | Messrs. John G. Stein and Co., Ltd. |
| Mr. T. R. LYNAM | Oughtibridge Silica Firebrick Co., Ltd. |
| Mr. H. OLIVER . | Derbyshire Silica Firebrick Co., Ltd. |
| Mr. H. PARNHAM | General Refractories, Ltd. (Worksop). |
| Dr. W. J. REES . | Department of Refractory Materials, The University, Sheffield. |
| Mr. T. F. E. RHEAD | City of Birmingham Gas Department. |
| Dr. T. SWINDEN | The United Steel Companies, Ltd. |
| Dr. A. E. J. VICKERS | Imperial Chemical Industries, Ltd. |
| Mr. A. T. GREEN | British Refractories Research Association. |
| Mr. A. E. DODD | British Refractories Research Association. |

# Section B. Steelworks Refractories.

## (I) The Work of the Open-hearth Refractories Joint Panel, 1939–1942.

The period under review has witnessed steady progress by the Panel. The field covered is best considered by splitting up the work into three sections, although it must be pointed out that each phase of the work has proceeded concurrently. Investigations on silica bricks have developed from a general survey to an intensive study of one roof; work on basic refractories has ranged from fundamental studies on the constitution of stabilised dolomite and chrome ores, to the preparation of test-sheets for the service testing of basic refractories in the open-hearth furnace; casting-pit refractories have several times been discussed in somewhat general terms, but now a sub-committee has been formed to deal with this side of the Panel's work. These three sections will be considered separately.

Early in 1939, Dr. Chesters (The United Steel Companies, Ltd.) presented to the Panel a preliminary survey of the factors influencing roof life in open-hearth furnaces. The properties of a number of brands of silica bricks were tabulated together with the life given by these bricks when used in an open-hearth roof. The three points suggested by this report were (a) the advantages of high bulk density for open-hearth roof bricks, (b) the usefulness of temperature control based on roof pyrometry, and (c) the necessity for careful warming up of both old and new roofs. Discussing this report, the Committee felt that while a high bulk density appears to be definitely desirable, its effect may in some cases be masked by other factors; thus it was suggested that two bricks of equal bulk density might have quite different pore structures and might consequently " season " at different rates. Following this preliminary survey, a commentary on open-hearth furnace roofs was prepared by Mr. Muir (Consett Iron Co., Ltd.); the principal factors which affect the life of a silica roof were considered to be furnace design, construction and operation, and the constitution and shape of the bricks. The results which had been obtained by the Consett Iron Co. with silica bricks to which no lime had been added were also outlined; these bricks were of very high refractoriness but were found to have glazed after one week's service. The

view was expressed that such glazing is a safety factor, since it reduces the surface area of the roof and reflects the heat back to the hearth. Data given on the physical properties of these silica bricks made without lime were as follows : refractoriness 1,750° C., porosity 20–22 per cent., cold crushing strength about 5,000 lb. per sq. in. It was emphasised by Mr. Muir that the conclusions he had reached were obtained in tests on basic furnaces. Acid furnace roofs were not considered suitable for testing refractories since the roof is seldom the limiting factor to the campaign ; the wear in an acid roof, moreover, proceeds in a manner quite different from the wear in a basic roof. For example, the joints in an acid roof do not glaze over so readily as those in a basic roof, so that the initial period of susceptibility to burning is much longer, usually five to six weeks.

The warming-up of open-hearth furnace roofs is now recognised as a period during which the silica bricks used in its construction may be very severely damaged. After the furnace has been success-fully gassed, there still remains a period of a few weeks during which the roof is not fully seasoned. The Committee discussed both these features of silica roof life at a meeting held in July, 1939. Mr. Hyslop (Messrs. J. G. Stein & Co., Ltd.) contributed a short note on the maturing of silica bricks in open-hearth furnace roofs ; it was considered that the rate of seasoning will depend on the com-position and texture of the brick, the composition of the dust and gases coming into contact with the brick, and the temperature. Rapid melting and " sweating " of the roof were thought to be brought about by such factors as a reducing atmosphere, or the presence of dusts rich in alumina or fluorspar. This problem was also dealt with in short memoranda prepared by Mr. Lynam (Oughtibridge Silica Firebrick Co., Ltd.) and Mr. Dodd (British Refractories Research Association). The main features affecting the behaviour of a silica brick in a steel furnace were considered to be the type of rock, grading, proportion of bond and mineraliser, and firing treatment used in its manufacture, and its shape and texture. The significance of the glazing of roof bricks was given full discussion by the Panel. It was agreed that a glazed roof should reflect heat rather than absorb it, but there was some difference of opinion as to whether a brick which will glaze readily is normally less refractory than a brick which remains matt. The possible influence of the nature of the raw quartzite on the ability of a brick to glaze was also considered. A report on the chemical and physical properties of some silica rocks used for brickmaking has since been presented to the Panel by the technical staff of General Refractories, Ltd. This report dealt with the features of quartzites in relation to their packing density after crushing and firing, the porosity of certain quartzites being shown to increase very considerably as a result of firing to silica brick kiln temperatures.

The earlier part of the discussions held by the Panel on the question of silica bricks for open-hearth furnace usage, made it clear that information was lacking on the conditions which actually obtain in a steel furnace at various periods in its operation. It was therefore decided to carry out a comprehensive piece of observational work on a selected roof. The United Steel Companies offered to install pyrometric equipment on one of their furnaces; The Oughtibridge Silica Firebrick Co. agreed to supply a roof, the manufacture of which had been followed through all its processes; the B.R.R.A. arranged to collaborate in the observational work while the roof was in gas, and to examine and test samples of the bricks before and after use. The work commenced shortly after the outbreak of war, the results obtained were ready for discussion by the Panel in January, 1941, and were published by The Iron and Steel Institute in November, 1941.* Since the data obtained are already available to members of the Institute, further discussion here is not necessary. It may be stated, however, that the work has done much to define the conditions to which silica bricks are likely to be subjected. Similar work at other plants would evidently be of great value in showing the variability of these conditions between different steelworks.

Turning to the programme carried out by the Panel on basic refractories, it may be stated that in July, 1939, the Committee felt that it should take steps to collect available information on the technical properties of basic refractories. Members of the staff of the B.R.R.A. therefore discussed problems associated with the use of basic refractories with a number of steelmakers. A report was prepared for the Panel in November, 1939. The information sought was confined to the purely technical aspect of the wider problem of furnishing the industry with adequate supplies of basic refractories in time of war. Hence, it was the concern of the Panel to obtain a cross-section of the experience of the steelmakers of this country with the newer types of basic materials. The Panel also made a collection of test data on basic refractories. Since these data referred to materials made before the outbreak of war, a useful standard was provided with which present-day basic refractories can be compared. The importance of making all the information on basic refractories available to the industry was keenly appreciated by the Panel, for it was considered imperative to provide all the known facts on the basic raw materials likely to be used in place of the Continental supplies now cut off. The B.R.R.A. therefore prepared a comprehensive review of basic refractory materials; this review, consisting of some two hundred pages, was published in *Bulletin* No. 56 of the B.R.R.A. in September, 1940. Concurrently with the collection and preparation of this report, the B.R.R.A. was carrying out fundamental work on the

* *Journal of the Iron and Steel Institute*, 1941, No. II., p. 203p.

constitution of fired dolomite clinkers and on the properties of the constituents of chrome and chrome-magnesite bricks. Four papers on the former topic are printed in full in the present report; the many papers on chrome refractories are summarised in Section D.

In addition to this planned research, the Panel has been called together on one or two occasions to consider specific problems requiring a rapid decision. Thus, in November, 1939, members of the Panel furnished replies to a questionnaire on the meaning to be attached to the terms " dead-burnt " and " hard-burnt " magnesite. The views and data supplied were given a preliminary discussion and were then passed to the Testing Committee of the B.R.R.A. to form a background against which to draw up a series of tentative standard methods of testing basic refractory raw materials and products. This work of the Testing Committee was completed and its recommendations were published in July, 1940. Complementary to the development of an agreed schedule of laboratory tests for basic refractories, discussion took place on the correct methods of carrying out service tests. This work was initiated as a result of views put forward by Mr. Muir (Consett Iron Co.), to the effect that the life of a basic brick in a steel furnace is considerably influenced by the method of construction and operation of the furnace. Other members of the panel agreed with this argument and discussion followed on the features of furnace design and operation most likely to influence the result of any service test. As a result of this work, a standard service test sheet was printed and is now in circulation.

The work of the Open-Hearth Panel on casting-pit refractories has developed considerably during the period under review. Plant work was carried out prior to the war to determine the factors which influence the life of ladle linings; this investigation has entailed the correlation of a considerable amount of data. Preliminary reports have been discussed by the Panel and the final detailed account of the work has now been completed. The Panel has also obtained a number of " Dando " American ladle bricks; these have been tested by the B.R.R.A. The bricks were notable for their perfect shape, low porosity (13 per cent.), low refractoriness (1,520° C.), and extraordinary bloating on firing to a temperature of 1,400° C. (permanent expansion of 34 per cent.).

The problem of the detection of refractory inclusions in steel, and the types of brick most liable to give rise to such inclusions, has also engaged the attention of the Committee. The method which it is proposed to use was first suggested by R. B. Sosman in a note which appeared in the *Bulletin of the American Ceramic Society* in 1939. The suggestion was here made that by impregnating the casting-pit refractories with a radio-active element, any inclusions arising from erosion of the refractories could be detected by their radio-active properties. Dr. Vickers (I.C.I., Ltd.) had

had experience in the use of this method of tracing small quantities of a substance, and Dr. Rees and Dr. Chesters collaborated with him in working out the preliminary details for an experiment to be made. The staff of the Physics Department of Sheffield University (Dr. Lawson assisted by the late Dr. Wilde) then helped in this work, and a set of casting-pit refractories is now being made preparatory to carrying out an actual test on a cast of steel.

A report on casting-pit refractories as a source of non-metallic inclusions in steel was presented to the British Ceramic Society by Dr. Rait (Messrs. Wm. Jessop & Sons, Ltd.) in September, 1941. A condensed report on the same subject has since been considered by the Open-Hearth Refractories Panel, which decided that the time was ripe for the setting up of a sub-committee to deal exclusively with casting-pit refractories. This sub-committee has held two meetings and has mapped out a considerable programme of work, including a survey of the range of sizes of casting-pit accessories now being produced. This survey is being made with a view to eliminating redundant sizes; if this were possible, it would lead to appreciable economies in the manufacturing processes and might enable more specialised methods of manufacture to be used.

This summary will give some indication of the general trend of the work carried out by the Open-Hearth Panel. A synopsis of the investigations made by the B.R.R.A. for the iron and steel industry will be found in Section D of the present Report.

# (2) A Study of the Reactions between Dolomite and Various Minerals.*

## Part I.—The Constitution of the Fired Clinkers.†

By J. R. RAIT, B.Sc., Ph.D., A.R.T.C., and A. T. GREEN, F.I.C.

ABSTRACT.

Moulded mixtures in various proportions of dolomite with flint, steatite, bentonite, china clay, olivine, serpentine, open-hearth slag, alumina, ferric oxide, zircon, baddeleyite, zirconia, rutile, chromite, and chromium oxide have been fired at about 1,500° C. Qualitative tests for the presence of free lime in the fired clinkers have been made and quantitative determinations carried out on numerous samples. Measurements have also been made of the index of hydration of the clinkers.

From a consideration of the relevant phase rule diagrams, assuming that the reactions in the clinkers had proceeded to equilibrium, the probable constitutions of the fired mixtures were calculated. The results of these calculations have been substantiated by (a) comparison of the calculated and experimentally determined free lime contents, (b) the dusting of those clinkers which calculation indicated contained a high percentage of calcium ortho-silicate, (c) by the form of the curves obtained on plotting the steam hydration indices against percentage of acidic oxides.

In all the clinkers it was assumed that the magnesia was present un-combined as periclase. With increasing addition of silica or siliceous minerals the evidence indicated the increasing combination of the lime to form, first, tricalcium silicate and, with larger silica contents, dicalcium silicate. There was evidence for the formation of $CaO.ZrO_2$ when zirconium minerals were added and of $2CaO.Cr_2O_3$ with chrome minerals.

INTRODUCTION.

Many attempts [1] have been made to utilise the very extensive deposits of dolomite [2] for the production of basic refractory bricks. Satisfactory bricks cannot be produced from calcined dolomite alone, due to the swelling and cracking accompanying the hydration of the free lime. It is well known that lime cannot be dead-burned at the temperatures available to industry, so that it has been found necessary to reduce the hydration by other methods. The chief method employed is to produce refractory and hydration-resistant compounds of lime. In modern practice a mixture of finely ground dolomite and a siliceous mineral is fired in a rotary kiln, the resulting clinker having a sufficiently low hydration tendency to allow of the production of bricks. Although it is known that the reduction in

TABLE I.—PERCENTAGE ANALYSES OF MATERIALS USED.

| | $CaO.$ | $SiO_2.$ | $Al_2O_3.$ | $Fe_2O_3.$ | $Cr_2O_3.$ | $ZrO_2.$ | $TiO_2.$ | $MgO.$ | Loss on Ignition. |
|---|---|---|---|---|---|---|---|---|---|
| Dolomite A | 50·50 | 3·22 | 1·04 | 3·06 | — | — | 0·20 | 34·94 | 6·64 |
| Dolomite B | 29·27 | 3·86 | 0·99 | 0·98 | — | — | 0·12 | 20·00 | 44·45 |
| Flint | — | 98·30 | — | — | — | — | — | — | 21·60 |
| Steatite A.T.1. | 0·60 | 36·90 | 1·34 | 6·40 | — | — | — | 32·70 | 4·40 |
| Steatite A | 0·34 | 60·76 | 1·08 | 1·01 | — | — | 0·55 | 31·59 | 8·35 |
| Steatite 3B | 0·81 | 46·18 | 10·72 | 2·06 | — | — | 0·48 | 29·73 | 16·33 |
| Steatite F.G.X.0. | 3·28 | 38·37 | 4·95 | 7·26 | — | — | 0·19 | 29·19 | 19·52 |
| Bentonite | 0·87 | 52·66 | 18·42 | 3·19 | — | — | — | 2·12 | 12·42 |
| China clay | 0·13 | 46·86 | 38·42 | 0·44 | — | — | 0·12 | 0·31 | 2·01 |
| Olivine | 0·26 | 40·34 | 2·22 | 6·09 | — | — | 0·18 | 48·98 | 13·24 |
| Serpentine | 0·33 | 31·01 | 3·72 | 10·06 | 6·22 | — | 1·92 | 35·30 | — |
| Acid open-hearth slag | 3·7 | 54·44 | 3·90 | MnO 17·6 / 17·8* | — | — | — | 0·42 | — |
| Alumina | — | — | 100 | — | — | — | — | — | — |
| Ferric oxide | — | — | — | 100 | — | — | — | — | — |
| Rutile | — | 1·18 | 1·29 | 2·25 | — | — | 95·96 | — | 0·14 |
| Zircon | — | 32·58 | — | 0·67 | — | 57·26 | 6·72 | — | 2·56 |
| Baddeleyite | — | 6·08 | 2·92 | 7·24 | — | 76·24 | 2·06 | — | — |
| Synthetic zircon | — | 32·86 | — | — | — | 67·14 | — | — | — |
| Zirconia | — | — | — | — | — | 100 | — | — | — |
| Chromite A | 0·58 | 7·40 | 10·84 | 12·93* | 41·56 | — | 0·30 | 21·24 | 4·46 |
| Chromite B | 0·22 | 10·46 | 12·52 | 17·24 | 32·34 | — | 0·22 | 21·82 | 4·30 |
| Chromium oxide | — | — | — | — | 100 | — | — | — | — |
| Synthetic chromite | — | — | — | 32·15* | 67·85 | — | — | — | — |

* FeO.

the hydration tendency is due to the formation of calcium silicates, the exact nature of the compounds formed remained a matter for conjecture. Further, although various types of siliceous minerals have been used by different workers,[1] it is difficult to compare their results, since different methods of measuring the hydration of dolomite clinker were employed. Hence it was decided to study the reactions between dolomite and various minerals, so that the products of the clinkering process could be determined and the relative efficiency of the various minerals examined.

EXPERIMENTAL PROCEDURE.

A survey of the literature revealed that the chief methods employed in the examination of clinkered dolomite were—

(a) mineralogical analysis by the petrological microscope ;
(b) hydration determinations ;
(c) free lime analysis ;
(d) mineralogical analysis by X-rays.

The procedure adopted in this work makes use of modified forms of (b) and (c) combined with the available thermal equilibrium data.

All the materials used were crushed, ground to pass 100-mesh sieve, sampled, and analysed. The analyses of the dolomites and stabilisers investigated are given in Table I. A series of mixes was prepared as follows : the dolomite and mineral were carefully weighed for each mix, ground together to produce efficient mixing, and then bonded with a solution of gum and water. (With dolomite A, which was calcined, it was necessary to use collodion as a bond.) The mix was then moulded into a cylinder by means of a steel mould and plunger. After drying, the mixes were fired, usually to about 1,500° C., on a pre-determined schedule in a gas-fired furnace. Observations were then made on the clinkers.

Details of the various series examined are given in Tables III, IV, VI, VII, and IX.

THE HYDRATION TEST.

(a) *Water Test.*

The first attempts to measure the hydration tendency of the various clinkers were based on the experiments of J. T. Robson and J. R. Withrow [3] and the later work of A. A. Chadeyron and W. J. Rees.[4] The clinker cylinders were placed in beakers containing distilled water maintained at 50° C. in a thermostatically controlled water-bath. Observations were made each day, but after a few weeks it was decided to discard this method. An example of the results obtained is shown in Table II.

(b) *Steam Hydration Test.*

A steam hydration test which proved very successful was then used. Approximately 5 gm. of clinker, crushed and ground to pass

a 100-mesh sieve, was placed in a porcelain crucible and subjected to the action of steam for 5 hours. After drying for about 2 hours in a hot air oven at 109° C., the crucible and contents were weighed and then calcined at 1,000° C. to constant weight.

TABLE II.—RESULTS OF WATER HYDRATION TEST ON DOLOMITE A—
SERPENTINE CLINKERS.

| Percentage Dolomite A. | Percentage Serpentine. | Observations. |
|---|---|---|
| 100 | 0 | Dusted after 21 hours. |
| 98 | 2 | ,, ,, 24 ,, |
| 95 | 5 | ,, ,, 28 ,, |
| 93 | 7 | ,, ,, 29 ,, |
| 90 | 10 | ,, ,, 43 ,, |
| 88 | 12 | ,, ,, 66 ,, |
| 85 | 15 | ,, ,, 100 ,, |
| 83 | 17 | ,, ,, 16 days. |
| 80 | 20 | Slight traces of hydration after few weeks. |
| 78 | 22 | ,, ,, |
| 75 | 25 | ,, ,, |
| 73 | 27 | ,, ,, |
| 70 | 30 | ,, ,, |

The Steam Hydration Index is denoted by :

$$\frac{W_1 - W_2}{W_2 - W} \times 100,$$

where W = weight of crucible, $W_1$ = weight of crucible+dry material, $W_2$ = weight of crucible+calcined material. As a result of a number of experiments, the reproducibility was found to be within ±2 per cent.

The Steam Hydration Indices were determined for each series by this method, the results obtained being included in Tables III, IV, VI, VII, and IX.

*The Hydration Curves.*

The hydration curves shown in Figs. 1–5 were obtained by plotting the steam hydration indices against the total percentage of acidic oxides. In this connection $Fe_2O_3$, $Al_2O_3$, and $Cr_2O_3$ as well as $SiO_2$, $TiO_2$, and $ZrO_2$ behave as acidic oxides. The acidic oxides present in the mixes combine with lime to form compounds which in most cases have lower hydration tendencies than lime itself. Consider curve 1 for dolomite and flint (Fig. 1). With increasing flint, the lime content is reduced by dilution; the free lime content is also reduced due to the formation of calcium compounds. Hence the hydration index decreases with increasing flint until all the CaO is combined. With further increase in flint a new phase in

place of free lime appears and a change in the variation of hydration index with acidic oxide content occurs. Hence, at the acidic oxide content at which all the lime is just combined, a change in the direction of hydration index–acidic oxide curve occurs. With further increase in flint, a change in the direction of the curve is
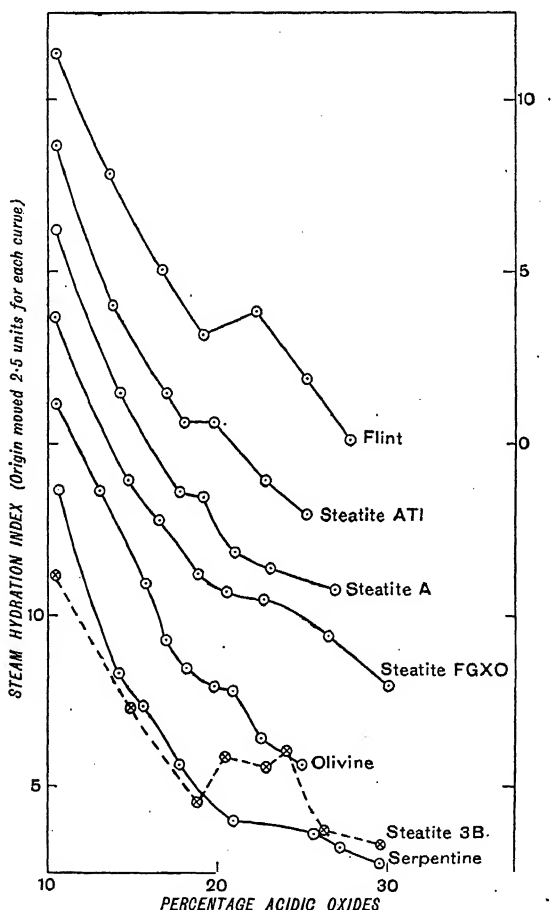


Fig. 1.—Relation between steam hydration index and percentage acidic oxides for clinkers prepared from dolomite B and various silicates.

probable, corresponding to a change in phase. It has been found that these changes in all the curves correspond to phase changes. The theory that the initial breaks in the hydration curves correspond to the composition at which there is just sufficient acidic oxides to combine with all the lime has been verified by means of White's free lime test (see Tables III, IV, VI, VII, and IX).
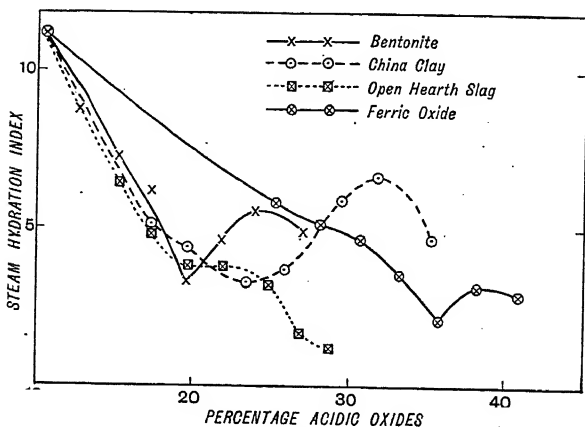
Fig. 2.—Relation between steam hydration index and percentage acidic oxides for clinkers prepared from dolomite B and bentonite, china clay, open-hearth slag, or ferric oxide.
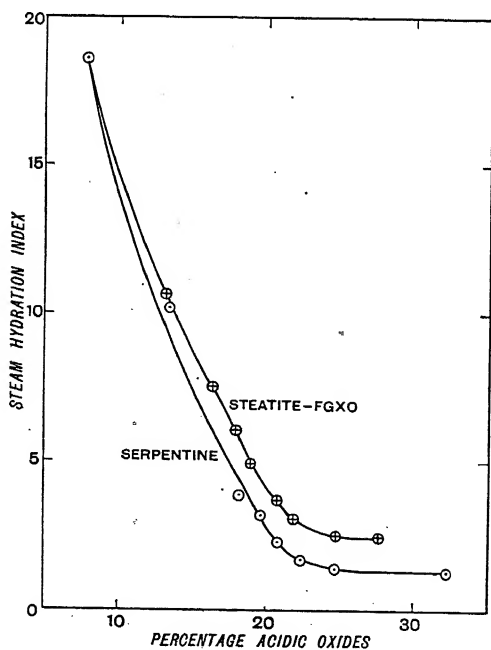


Fig. 3.—Relation between steam hydration index and percentage acidic oxides for clinkers prepared from dolomite A and steatite or serpentine.

THE QUALITATIVE FREE LIME TEST.

A. H. White [5] developed an optical test for the detection of free lime in Portland cement, using a mineralogical microscope. The test is carried out as follows : a small amount of the finely ground
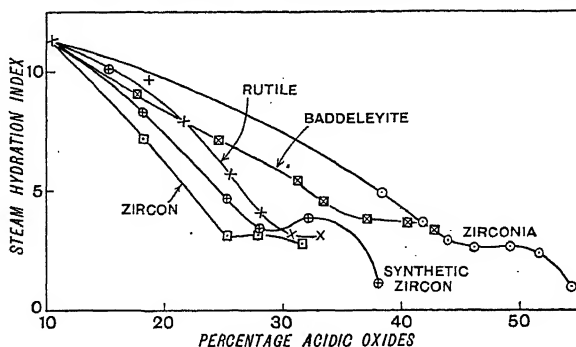


Fig. 4.—Relation between steam hydration index and percentage acidic oxides for clinkers prepared from dolomite B and various zirconium or titanium compounds.
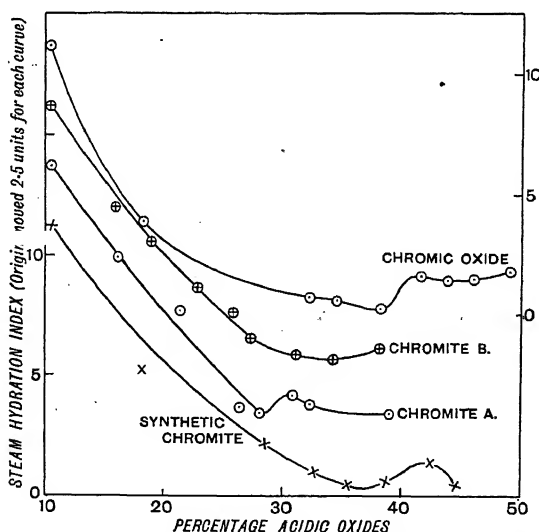


Fig. 5.—Relation between steam hydration index and percentage acidic oxides for clinkers prepared from dolomite B and various chromium compounds.

sample is placed on a glass slide and wetted with a solution consisting of 5 gm. phenol dissolved in 5 c.c. nitrobenzene with the addition of two drops of water. The slide is then examined between crossed nicols, using a magnification of about 100. The presence of

PLATE I.

Fig. 6 (*a–f*).—Photomicrographs illustrating White's test for free lime (crossed nicols, × 100).
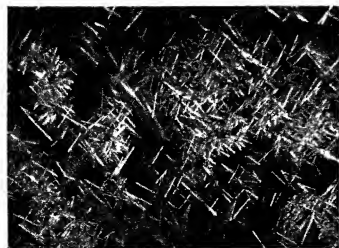
(*a*) 100 per cent. dolomite B.
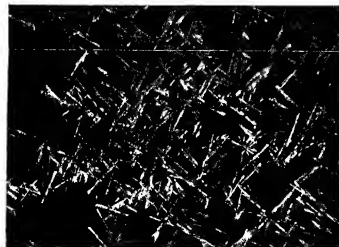
(*b*) 90 per cent. dolomite B and 10 per cent. olivine.

(*c*) 88 per cent. dolomite B and 12 per cent. olivine.

(*d*) 85 per cent. dolomite B and 15 per cent. olivine.
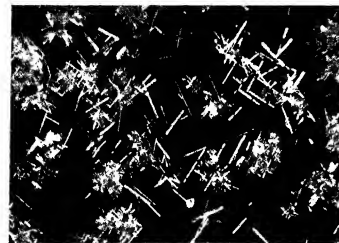
(*e*) 96 per cent. dolomite B and 4 per cent. flint.
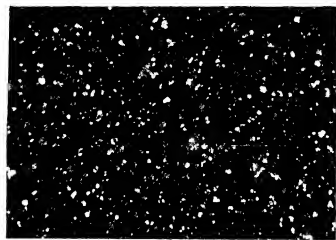
(*f*) 94·3 per cent. dolomite B and 5·7 per cent. flint.
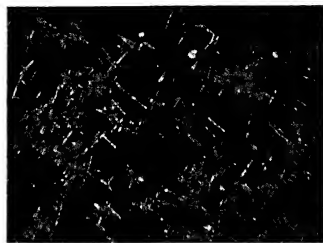
(*g*) 88 per cent. dolomite B and 12 per cent. steatite F.G.X.O.

(*h*) 85 per cent. dolomite B and 15 per cent. steatite F.G.X.O.
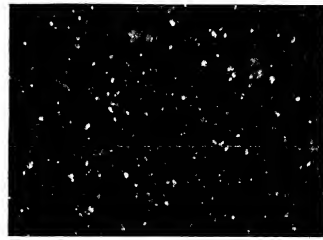
(*i*) 73 per cent. dolomite A and 27 per cent. serpentine.

(*j*) 70 per cent. dolomite A and 30 per cent. serpentine.

[*To face page* 20]

free lime is shown by long, highly bi-refringent needles which radiate from the free lime particles.    When the free lime content is appreciable these needles spread rapidly over the surface of the slide, but. to detect traces of free lime the slide should be examined about an hour after preparation.    W. C. Reibling and F. D. Reyes [6] confirmed this test and it has been recently stated [7] that, although there appears to be a slight attack of other constituents in some substances, there is no interference with the test.    Small quantities of free lime in materials such as sand lime bricks or unhydrated cements have been determined quantitatively by this method.

Each series of dolomite-stabiliser mixes was examined in this way, and as shown in Tables III, IV, VI, VII, and IX it was possible to determine the composition, within very close limits, for each series, at which there was just sufficient acidic oxides to combine with all the lime.    In each series the test indicated decreasing free lime contents.    A few photomicrographs of these tests are shown in Fig. 6 (Plate I).

THE CONSTITUTION OF THE VARIOUS MIXES.

It was found convenient to classify the various dolomite mixes into four groups for the study of the constitution.

    (1) Dolomite B and (a) flint, (b) steatite A.T.I., (c) steatite A, (d) steatite F.G.X.O., (e) steatite 3B, (f) olivine, (g) serpentine, (h) bentonite, (i) china clay, (j) ferric oxide, and (k) alumina ; dolomite A and (a) steatite F.G.X.O. and (b) serpentine.

    (2) Dolomite B and acid open-hearth slag.

    (3) Dolomite B and (a) zirconia, (b) synthetic zircon, (c) baddeleyite, (d) rutile.

    (4) Dolomite B and (a) chromium oxide ($Cr_2O_3$), (b) synthetic chromite, (c) chromite A, (d) chromite B.

*Group* 1.

All the calcined mixes in group 1 consist of lime, silica, alumina, ferric oxide, and magnesia.    Two interesting features were noted.

    (a) In all cases the initial break in the hydration curve corresponding to the composition at which there was just sufficient acidic oxides to combine with all the lime, occurred at a $CaO/SiO_2$ ratio equal to 3 approximately.

    (b) The dusting phenomenon which is due to the expansion accompanying the transformation from $\beta \rightarrow \gamma$ $2CaO.SiO_2$ [8] also occurred at an approximately constant $CaO/SiO_2$ ratio equal to 2·2.

This evidence indicated that the chemical reactions had attained equilibrium.    Hence it was decided to study the various appropriate thermal equilibrium diagrams in order to find whether the constitution of the various mixes could thus be determined.

A number of these diagrams, including that of the CaO–MgO–SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$ system, have not been determined, as is shown by reference to the compilation of thermal equilibrium diagrams made by F. P. Hall and H. Insley.[9]   However, examination of the available data revealed that it could be safely assumed that in all the calcined mixes in group 1 the magnesia would crystallise out as periclase.   For example, examination of the CaO–MgO–SiO$_2$ system shows that in the range of compositions of the mixes of group 1, magnesia will be present as periclase.   A similar conclusion is drawn
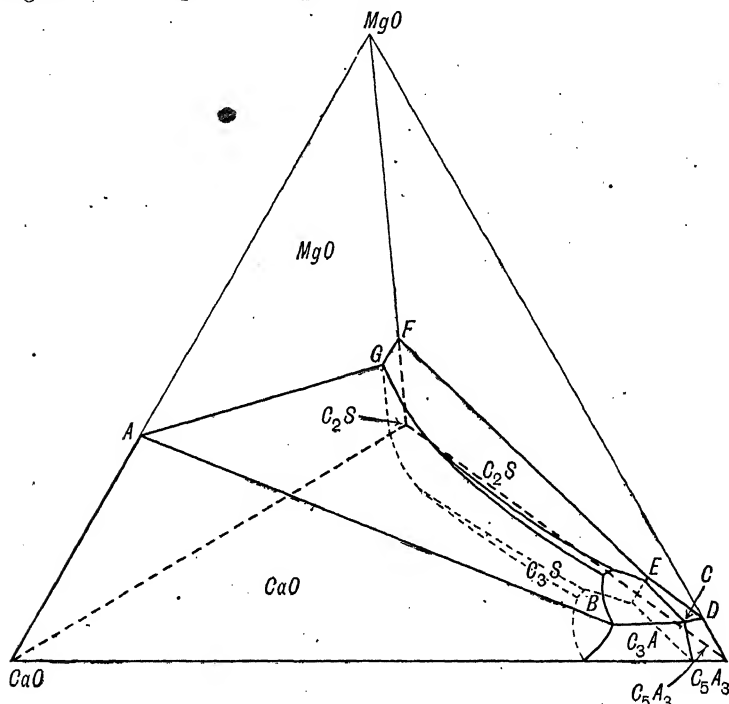


Fig. 7.—The quaternary system CaO–MgO–2CaO.SiO$_2$–5CaO.3Al$_2$O$_3$ (after H. F. McMurdie and H. Insley, *Bur. Standards J. Research*, **16**, 467, 1936).

from examination of the quaternary systems.   (*See,* for example, the diagram of the CaO–MgO–2CaO.SiO$_2$–5CaO.3Al$_2$O$_3$ system shown in Fig. 7.)
    Provided this assumption is correct, a study of the quaternary diagram CaO–SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$ should indicate the constitution of these mixes.   The complete quaternary system has not yet been worked out.   However, complete data on the ternary system CaO–SiO$_2$–Al$_2$O$_3$ have been published by G. A. Rankin and F. E. Wright [10] ; part of the ternary system CaO–Al$_2$O$_3$–Fe$_2$O$_3$ has been

investigated by W. C. Hansen, L. T. Brownmiller, and R. H. Bogue,[11] while W. C. Hansen and R. H. Bogue [12] have indicated the products of final crystallisation in the high lime portion of the system.

G. A. Rankin and F. E. Wright [10] proved that the three compounds CaO, 2CaO.SiO$_2$, and 5CaO.3Al$_2$O$_3$ form a true ternary system within the larger system CaO–SiO$_2$–Al$_2$O$_3$. F. M. Lea and
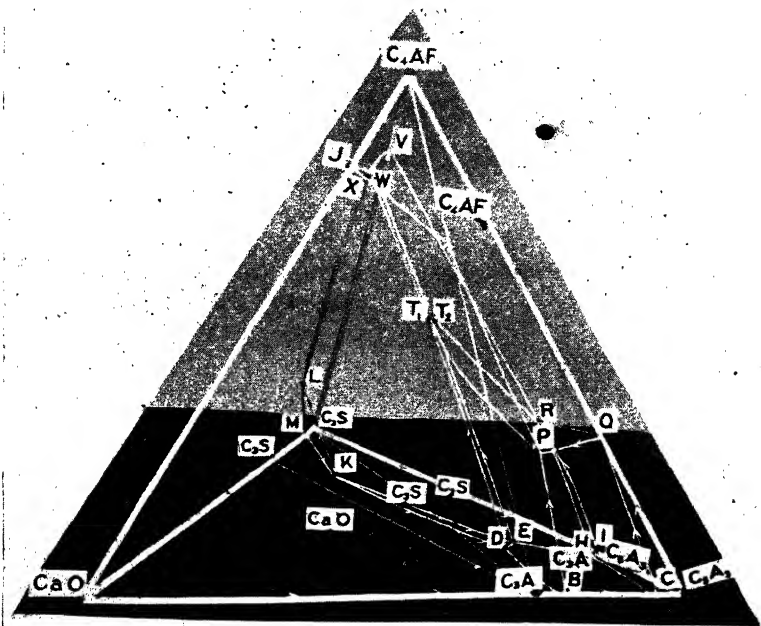


Fig. 8 (a).—The quaternary system CaO–2CaO.SiO$_2$–5CaO.3Al$_2$O$_3$–4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ (after F. M. Lea and T. W. Parker).[13]
The complete tetrahedron.

T. W. Parker [13] also pointed out that the compounds CaO, 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, and 5CaO.3Al$_2$O$_3$ form a true ternary system within the larger system CaO–Al$_2$O$_3$–Fe$_2$O$_3$. Further, since W. C. Hansen and R. H. Bogue [12] have shown that no ternary compounds are to be expected in the system CaO–SiO$_2$–Fe$_2$O$_3$, F. M. Lea and T. W. Parker[13] concluded that a true quaternary system might be formed by the four compounds CaO, 2CaO.SiO$_2$, 5CaO.3Al$_2$O$_3$, and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$. F. M. Lea and T. W. Parker [13] proved this to be so by investigation and have obtained complete data for this quaternary system.

Examination of the compositions of group 1 reveals that

neglecting MgO the majority of these fall within the quaternary system $CaO–2CaO.SiO_2–4CaO.Al_2O_3.Fe_2O_3–5CaO.3Al_2O_3$. Hence it was considered possible to work out the constitution of these mixes with the aid of this diagram. For complete data on this quaternary system, the work of F. M. Lea and T. W. Parker,[13] should be consulted, but sufficient data are shown in Fig. 8 to enable this
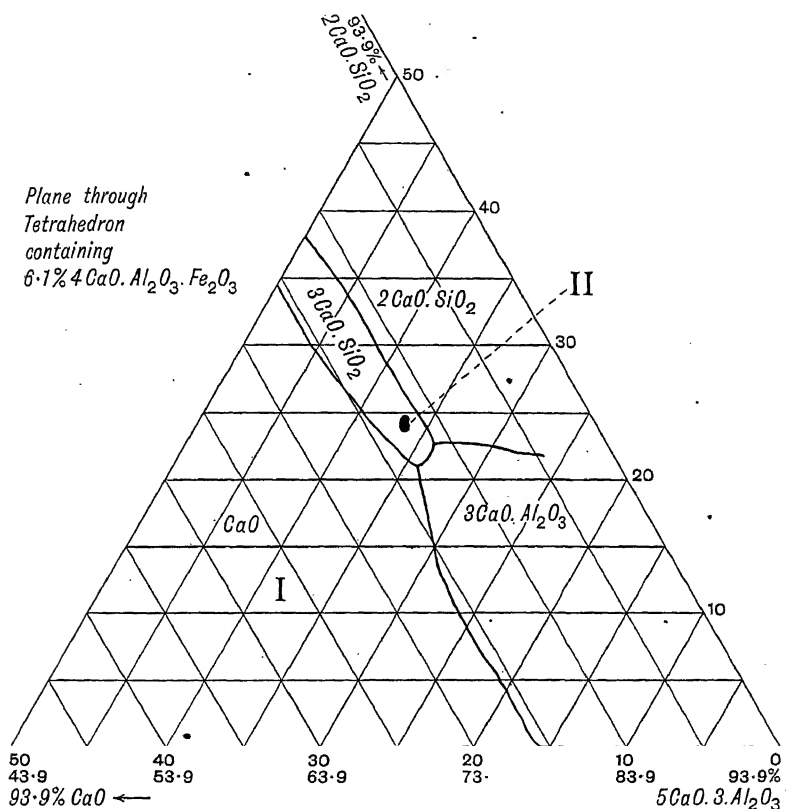


Fig. 8 (b).—The quaternary system $CaO–2CaO.SiO_2–5CaO.3Al_2O_3–$
$4CaO.Al_2O_3.Fe_2O_3$ (after F. M. Lea and T. W. Parker).[13]
The plane through the tetrahedron containing 6·1 per cent.
$4CaO.Al_2O_3.Fe_2O_3$.

method of calculation of the constitution of the mixes to be explained.

The method of calculation of a typical case will be given in detail, viz. dolomite B and steatite F.G.X.O. (*see* Table III, page 26). The compositions of fired mixes having up to 12 per cent. steatite lie within the field of primary crystallisation of CaO, such as in area 1 of Fig. 8 (b). From a study of these diagrams it is obvious that the other phases to be found are $3CaO.SiO_2, 3CaO.Al_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$.

Consider, for example, the mix with 5 per cent. of steatite. The fired percentage composition was CaO, 49·11 ; SiO$_2$, 9·81 ; Al$_2$O$_3$, 2·09 ; Fe$_2$O$_3$, 2·27 ; MgO, 35·90. It is assumed that all the magnesia crystallises as *periclase*. Thus the percentage (by weight) present =35·9. All the Fe$_2$O$_3$ is assumed to combine with CaO and Al$_2$O$_3$ to form 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$. Thus 2·27 gm. of Fe$_2$O$_3$ will combine with : $\dfrac{102 \times 2·27}{160}$ gm. A and $\dfrac{224 \times 2·27}{}$ CaO, 1·45 Al$_2$O$_3$ and 3·18 gm. CaO. Hence percentage by weight of $4CaO.Al_2O_3.Fe_2O_3 = 3·18 + 1·45 + 2·27 = 6·9$. The remaining alumina is assumed to combine to form 3CaO.Al$_2$O$_3$. Thus (2·09–1·45) gm. Al$_2$O$_3$ combine with $\dfrac{168 \times 0·64}{102} = 1·05$ gm. of CaO. Hence the percentage by weight of $3CaO.Al_2O_3 = 1·05 + 0·64 = 1·69$.

All the silica is assumed to combine with lime to form 3CaO.SiO$_2$. Thus 9·81 gm. SiO$_2$ combine with $\dfrac{168 \times 9·81}{60} = 27·47$ gm. of CaO. Hence the percentage by weight of $3CaO.SiO_2 = 27·47 + 9·81 = 37·28$. The free lime is calculated by difference between the total and combined lime. In this case the percentage *free lime* will be 49·11 – (27·47 + 1·05 + 3·18) = 17·41.

The compositions of fired mixes containing 15 and 20 per cent. steatite are in field II of Fig. 8 (*b*). Hence the phases in these test clinkers will be 3CaO.SiO$_2$, 2CaO.SiO$_2$, 3CaO.Al$_2$O$_3$, 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, and MgO. Consider the mix with 15 per cent. steatite. Its percentage composition when fired was : CaO, 42·44 ; SiO$_2$, 15·12 ; Al$_2$O$_3$, 2·65 ; Fe$_2$O$_3$, 3·22 ; MgO, 35·77.

The percentage of *periclase* is assumed to be 35·77. The calculation is made as previously, 4·51 and 2·05 gm. of CaO and Al$_2$O$_3$ respectively being found necessary to combine with 3·22 gm. Fe$_2$O$_3$. Thus the percentage weight of $4CaO.Al_2O_3.Fe_2O_3 = 4·51 + 2·05 + 3·22 = 9·78$.

0·99 gm. CaO is required to combine with (2·65–2·05) gm. Al$_2$O$_3$ to form tri-calcium aluminate. Thus the percentage weight of $3CaO.Al_2O_3$ is 0·99 + 0·60 = 1·59.

The silica is assumed to combine with all the remaining lime to form 3CaO.SiO$_2$ and 2CaO.SiO$_2$. The percentage of lime available is 42·44 – 4·51 – 0·99 = 36·94. Let $x$ be the percentage of silica combined as 3CaO.SiO$_2$, then $\dfrac{168x}{60} + \dfrac{(15·12 - x) \times 112}{60} = 36·94$, whence $x = 9·34$ and the percentage by weight of =35·49 and the percentage by weight of $\times (15·12 - 9·34) = 16·57$.

In a similar fashion the constitutions of the majority of the series in group 1 were calculated. However, there are a number of cases whose compositions do not fall within the quaternary system CaO–2CaO.SiO$_2$–4CaO.Al$_2$O$_3$.Fe$_2$O$_3$–5CaO.3Al$_2$O$_3$. These,

however, lie on the $CaO$–$SiO_2$–$Fe_2O_3$ side of the compound $4CaO.Al_2O_3.Fe_2O_3$ in the major system $CaO$–$SiO_2$–$Al_2O_3$–$Fe_2O_3$. To illustrate the method of calculation in such a case, consider the series dolomite A—steatite F.G.X.O. (Table IV, page 28). From consideration of the available data on the $CaO$–$Fe_2O_3$ and $CaO$–$Fe_2O_3$–$SiO_2$ diagrams, it may be shown that $CaO$, $2CaO.Fe_2O_3$, $3CaO.SiO_2$ and $4CaO.Al_2O_3.Fe_2O_3$ crystallise out from the high lime melts. W. C. Hansen and R. H. Bogue [12] have shown that no ternary compound in the $CaO$–$SiO_2$–$Fe_2O_3$ diagram is to be expected. Hence those clinkers which show free $CaO$ will probably contain the following compounds in addition : $4CaO.Al_2O_3.Fe_2O_3$, $2CaO.Fe_2O_3$, $3CaO.SiO_2$, and $MgO$. Consider, for example, the fired mix, of percentage analysis : $CaO$ 47·24, $SiO_2$ 9·24, $Fe_2O_3$ 4·01, $Al_2O_3$ 1·77, $MgO$ 37·07.

The percentage by weight of *periclase* is assumed to be 37·07.

1·77 gm. of $Al_2O_3$ require 3·89 gm. of $CaO$ and 2·78 gm. of $Fe_2O_3$ to form $4CaO.Al_2O_3.Fe_2O_3$. The percentage by weight calculated to be present is therefore 8·44.

(4·01—2·78) gm. of $Fe_2O_3$ require 0·86 gm. of $CaO$ to form $2CaO.Fe_2O_3$. The percentage calculated to be present is therefore 2·09.

·24 gm. of silica require 25·87 gm. of $CaO$ to form $3CaO.SiO_2$. The percentage calculated present is 35·11.

The percentage *free lime* present is calculated as 47·24—3·89 —0·86—25·87=16·62.

Hence it was possible to calculate the constitution of all the series in group 1. The constitutions of a selection of the various series are given in Tables III and IV (*see* pages 26–29).

Two methods of checking the accuracy of these calculations of constitution of the various series of group 1 were available :

.(*a*) The " dusting " of certain clinkers on cooling is due to the expansion accompanying the $\beta \rightarrow \gamma$ transformation of $2CaO.SiO_2$ at 675° C.[8] Examination of Tables III and IV reveals that " dusting " only occurred when there was a high proportion of $2CaO.SiO_2$ present. Fig. 9 is a photograph of a typical series.

(*b*) Comparison of the calculated amounts of free lime with the experimentally determined free lime.
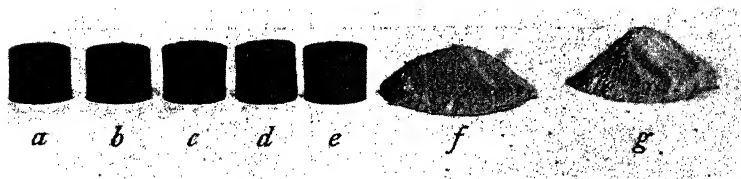


Fig. 9.—Condition of dolomite B–steatite A.T.1 mixes after firing.

TABLE III.—DATA ON THE CONSTITUTION OF DOLOMITE CLINKERS FIRED TO 1,530° C. FOR 3 HOURS.

| Dolomite, per cent. | Stabiliser, per cent. | Ultimate Analysis of Clinker, per cent. | | | | | Calculated Mineralogical Composition (Weight, per cent.). | | | | | | | | White's Test for Free Lime. | Steam Hydration Index, per cent. | Description of Clinker. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CaO$. | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | $MgO$. | Periclase, $MgO$. | Free Lime. | $3CaO.SiO_2$. | $4CaO.Al_2O_3.Fe_2O_3$. | $3CaO.Al_2O_3$. | $5CaO.3Al_2O_3$. | $2CaO.SiO_2$. | $2CaO.Fe_2O_3$. | | | |
| B 100 | — | 52·6 | 6·9 | 1·8 | 1·8 | 36·0 | 36·0 | 29·6 | 26·4 | 5·4 | 1·7 | — | — | — | + | 11·2 | Black-brown solid. |
| B 98 | Flint. 2 | 50·8 | 10·2 | 1·7 | 1·7 | 34·7 | 34·7 | 18·9 | 38·7 | 5·2 | 1·7 | — | — | — | + | 7·8 | Black-brown solid. |
| 96 | 4 | 49·0 | 13·3 | 1·7 | 1·6 | 33·5 | 33·5 | 8·4 | 50·7 | 5·0 | 1·6 | — | — | — | + | 5·1 | ,, ,, ,, |
| 94·3 | 5·7 | 47·5 | 15·9 | 1·6 | 1·6 | 32·5 | 32·5 | — | 59·2 | 4·8 | 1·6 | — | 1·0 | — | — | 3·2 | Black-brown solid with a few dust spots. |
| 92 | 8 | 45·5 | 19·3 | 1·5 | 1·5 | 31·1 | 31·1 | — | 26·1 | 4·6 | 1·5 | — | 35·7 | — | — | 3·8 | Completely dusted on cooling. |
| 90 | 10 | 43·9 | 22·2 | 1·5 | 1·5 | 30·0 | 30·0 | — | — | 4·5 | — | 1·1 | 63·0 | — | — | 1·8 | ,, ,, ,, |
| B 95 | Steatite A.T.I. 5 | 49·1 | 9·7 | 1·8 | 2·2 | 36·4 | 36·4 | 18·1 | 37·0 | 6·7 | 1·0 | — | — | — | + | 6·5 | Brown-black solid. |
| 88 | 12 | 44·2 | 13·4 | 1·8 | 2·8 | 36·9 | 36·9 | 2·7 | 51·0 | 8·4 | — | — | — | 0·04 | + | 3·1 | ,, ,, ,, ,, |
| 85 | 15 | 42·2 | 14·9 | 1·8 | 3·0 | 37·1 | 37·1 | — | 42·3 | 8·4 | — | — | 10·9 | 0·5 | — | 3·1 | ,, ,, ,, ,, |
| 83 | 17 | 40·9 | 15·8 | 1·8 | 3·2 | 37·3 | 37·3 | — | 29·5 | 8·4 | — | — | 22·9 | 0·8 | — | — | ,, ,, ,, ,, |
| 80 | 20 | 38·9 | 17·4 | 1·8 | 3·4 | 37·4 | 37·4 | — | 8·5 | 8·4 | — | — | 43·5 | 1·1 | — | 1·4 | Completely dusted on cooling. |

| B | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Steatite A. | | | | | | | | | | | | | | | | |
| 96 | 4 | 49·2 | 10·7 | 1·7 | 1·7 | 35·8 | 35·8 | 15·6 | 40·8 | 5·2 | 1·7 | — | — | — | + | 6·5 | Black-brown solid. |
| 92 | 8 | 45·8 | 14·3 | 1·7 | 1·7 | 35·6 | 35·6 | 4·0 | 52·7 | 5·1 | 1·7 | — | — | — | + | 3·6 | Yellow-brown black solid. |
| 90 | 10 | 44·2 | 16·0 | 1·7 | 1·7 | 35·5 | 35·5 | — | 44·6 | 5·0 | 1·7 | 12·2 | — | — | − | 3·5 | ,, ,, ,, |
| 88 | 12 | 42·7 | 17·7 | 1·6 | 1·7 | 35·4 | 35·4 | — | 25·7 | 4·9 | 1·7 | 31·4 | — | — | − | 2·0 | ,, ,, ,, |
| 85 | 15 | 40·4 | 20·1 | 1·6 | 1·6 | 35·3 | 35·3 | — | — | 4·9 | 0·1 | 57·7 | 1·1 | — | − | 1·4 | Completely dusted on cooling. |
| B | Steatite F.G.X.O. | | | | | | | | | | | | | | | | |
| 95 | 5 | 49·1 | 9·8 | 2·1 | 2·3 | 35·9 | 35·9 | 17·4 | 37·3 | 6·9 | 1·7 | — | — | — | + | 6·4 | Black solid. |
| 90 | 10 | 45·7 | 12·5 | 2·4 | 2·8 | 35·8 | 35·8 | 5·8 | 47·6 | 8·4 | 1·6 | — | — | — | + | 3·6 | ,, ,, |
| 88 | 12 | 44·4 | 13·6 | 2·5 | 2·9 | 35·8 | 35·8 | 1·2 | 51·6 | 8·9 | 1·6 | — | — | — | + | 3·2 | Black solid with few dust spots. |
| 85 | 15 | 42·4 | 15·1 | 2·7 | 3·2 | 35·8 | 35·8 | — | 35·5 | 9·8 | 1·6 | 16·6 | — | — | − | 3·0 | Black solid with increase in number of dust spots. |
| 80 | 20 | 39·3 | 17·6 | 2·9 | 3·7 | 35·7 | 35·7 | — | 1·8 | 11·1 | 1·5 | 49·1 | — | — | − | 2·0 | Completely dusted on cooling. |
| B | Steatite 3B. | | | | | | | | | | | | | | | | |
| 95 | 5 | 48·6 | 10·4 | 2·6 | 1·8 | 35·7 | 35·7 | 14·5 | 39·6 | 5·5 | 3·8 | — | — | — | + | 7·8 | Black solid. |
| 90 | 10 | 44·7 | 13·7 | 3·3 | 1·8 | 35·5 | 35·5 | 0·3 | 52·0 | 5·6 | 5·6 | — | — | — | + | 4·7 | ,, ,, ,, |
| 88 | 12 | 43·2 | 14·9 | 3·6 | 1·9 | 35·4 | 35·4 | — | 35·5 | 5·6 | 6·4 | 16·0 | — | — | − | 5·9 | ,, ,, ,, |
| 85 | 15 | 41·9 | 16·7 | 4·0 | 1·9 | 35·3 | 35·3 | — | 13·9 | 5·7 | 7·5 | 37·5 | — | — | − | 5·7 | ,, ,, ,, |
| 83 | 17 | 39·6 | 17·9 | 4·3 | 1·9 | 35·2 | 35·2 | — | — | 5·7 | 2·4 | 51·4 | 4·2 | 0·2 | − | 6·0 | Completely dusted on cooling. |
| B | Olivine. | | | | | | | | | | | | | | | | |
| 96 | 4 | 49·1 | 9·3 | 1·8 | 2·1 | 37·0 | 37·0 | 19·4 | 35·3 | 6·3 | 1·3 | — | — | — | + | 8·7 | Grey-black solid. |
| 92 | 8 | 45·7 | 11·7 | 1·9 | 2·4 | 37·9 | 37·9 | 8·9 | 44·6 | 7·2 | 1·0 | — | — | — | + | 6·0 | ,, ,, ,, |
| 90 | 10 | 44·1 | 12·6 | 1·9 | 2·5 | 38·3 | 38·3 | 5·0 | 47·7 | 7·6 | 0·7 | — | — | — | + | 4·3 | ,, ,, ,, |
| 88 | 12 | 42·5 | 13·6 | 1·9 | 2·6 | 38·7 | 38·7 | 0·1 | 51·6 | 8·0 | 0·6 | — | — | — | + | 3·4 | ,, ,, ,, |
| 85 | 15 | 40·3 | 15·1 | 1·9 | 2·8 | 39·3 | 39·3 | — | 32·7 | 8·6 | 0·3 | 18·5 | — | — | − | 2·9 | Grey-black with a number of brown dust spots. |
| 83 | 17 | 38·8 | 16·0 | 1·9 | 2·9 | 39·7 | 39·7 | — | 19·0 | 8·9 | 0·1 | 31·6 | — | — | − | 2·8 | Large number of dust spots. |
| 80 | 20 | 36·6 | 17·4 | 1·9 | 3·2 | 40·3 | 40·3 | — | — | 9·2 | — | 48·3 | — | — | − | 1·4 | Completely dusted. |

3

TABLE IV.—DATA ON THE CONSTITUTION OF DOLOMITE CLINKERS.

| Dolomite, per cent. | Stabiliser, per cent. | Ultimate Analysis of Clinker, per cent. | | | | | | Calculated Mineralogical Composition (Weight, per cent.). | | | | | | | | | White's Free Lime Test. | Steam Hydration Index, per cent. | Firing T Treatment, 3 hours at (°C.) | Description of Clinker. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CaO.$ | $SiO_2.$ | $Al_2O_3.$ | $Fe_2O_3.$ | $Cr_2O_3.$ | $MgO.$ | Periclase, $MgO.$ | Free Lime. | $3CaO.SiO_2.$ | $4CaO.Al_2O_3.Fe_2O_3.$ | $3CaO.Al_2O_3.$ | $5CaO.3Al_2O_3.$ | $2CaO.SiO_2.$ | $2CaO.Fe_2O_3.$ | $2CaO.Cr_2O_3.$ | | | | |
| B 100 | — | 52·6 | 6·9 | 1·8 | 1·8 | — | 36·0 | 36·0 | 29·6 | 26·4 | 5·4 | 1·7 | — | — | — | — | + | 11·2 | 1,530 | — |
| 95 | Serpentine. 5 | 48·7 | 9·1 | 2·0 | 2·5 | 0·54 | 36·3 | 36·3 | 18·6 | 34·7 | 7·6 | 1·0 | — | — | — | 1·0 | + | 5·8 | 1,530 | Black solid. |
| 93 | 7 | 47·2 | 10·0 | 2·1 | 2·8 | 0·75 | 36·6 | 36·6 | 14·4 | 37·9 | 8·5 | 0·7 | — | — | — | 1·3 | + | 4·9 | | ,, ,, |
| 90 | 10 | 45·0 | 11·2 | 2·1 | 3·2 | 1·1 | 36·7 | 36·7 | 8·2 | 42·6 | 9·7 | 0·3 | — | — | — | 1·8 | + | 3·1 | | ,, ,, |
| 88 | 12 | 43·5 | 12·0 | 2·2 | 3·5 | 1·3 | 36·8 | 36·8 | 4·1 | 45·6 | 10·6 | — | — | — | — | 2·2 | — | 3·2 | | ,, ,, |
| 85 | 15 | 41·4 | 13·2 | 2·3 | 3·9 | 1·6 | 37·0 | 37·0 | — | 43·5 | 10·8 | — | — | 4·9 | 0·4 | 2·7 | — | 3·2 | | ,, ,, |
| 80 | 20 | 38·0 | 15·0 | 2·5 | 4·5 | 2·0 | 37·3 | 37·3 | — | 10·4 | 11·8 | — | — | 35·2 | 1·1 | 3·5 | — | 1·5 | | Partly dusted. |
| B 96 | Bentonite. 4 | 49·7 | 10·3 | 3·0 | 1·9 | — | 34·1 | 34·1 | 15·3 | 39·1 | 5·7 | 4·7 | — | — | — | — | + | 7·4 | 1,530 | Black solid. |
| 94 | 6 | 48·3 | 11·9 | 3·6 | 2·0 | — | 33·3 | 33·2 | 8·4 | 45·2 | 5·9 | 6·1 | — | — | — | — | + | 6·2 | | ,, ,, |
| 92 | 8 | 46·9 | 13·5 | 4·1 | 2·1 | — | 32·3 | 32·3 | 1·7 | 51·3 | 6·3 | 7·5 | — | — | — | — | + | 3·2 | | ,, ,, |
| 90 | 10 | 45·4 | 15·1 | 4·7 | 2·1 | — | 31·4 | 31·4 | — | 35·9 | 6·3 | 9·0 | — | 16·1 | — | — | — | 4·7 | | Black solid showing a few dust spots. |
| 88 | 12 | 44·2 | 16·6 | 5·3 | 2·1 | — | 30·5 | 30·5 | — | 15·4 | 6·5 | 10·3 | — | 34·8 | — | — | — | 5·6 | | ,, ,, |
| 85 | 15 | 42·2 | 18·9 | 6·1 | 2·2 | — | 29·2 | 29·2 | — | — | 6·7 | — | 9·0 | 51·7 | — | — | — | 5·0 | 1,530 | Completely dusted on cooling. |

| | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| B | China clay | | | | | | | | | | | | | | | | | | | |
| 95 | 5 | 48.7 | 10.5 | 5.0 | 1.7 | — | 33.3 | 33.3 | 10.4 | 40.0 | 5.1 | 10.5 | — | — | — | — | + | 5.1 | 1,350 | Brown-black solid. |
| 93 | 7 | 47.1 | 11.9 | 6.3 | 1.6 | — | 32.2 | 32.2 | 3.0 | 45.2 | 5.0 | 13.8 | — | — | — | — | + | 4.5 | | ,, ,, |
| 90 | 10 | 44.9 | 13.9 | 8.1 | 1.6 | — | 30.7 | 30.7 | — | 20.7 | 4.8 | 18.7 | — | 24.2 | — | — | — | 3.3 | | Brown-black vitreous solid. |
| 88 | 12 | 43.4 | 15.2 | 9.2 | 1.5 | — | 29.7 | 29.7 | — | — | 4.7 | 19.4 | 1.8 | 43.5 | — | — | — | 3.7 | | Brown-black solid. |
| B | Ferric Oxide. | | | | | | | | | | | | | | | | | | | |
| 90 | 10 | 43.9 | 5.8 | 1.5 | 18.1 | — | 30.0 | 30.0 | 13.4 | 22.0 | 7.1 | — | — | — | 26.9 | — | + | 5.7 | 1,450 | Black vitrified solid. |
| 86 | 14 | 40.8 | 5.4 | 1.4 | 24.0 | — | 27.8 | 27.8 | 7.4 | 20.4 | 6.6 | — | — | — | 37.2 | — | + | 4.7 | | ,, ,, ,, |
| 84 | 16 | 39.2 | 5.2 | 1.3 | 26.9 | — | 26.8 | 26.8 | 4.6 | 19.7 | 6.3 | — | — | — | 42.1 | — | + | 3.6 | | ,, ,, ,, |
| 82 | 18 | 37.8 | 5.0 | 1.3 | 29.6 | — | 25.9 | 25.9 | 1.7 | 18.9 | 6.1 | — | — | — | 46.9 | — | — | 2.1 | | ,, ,, ,, |
| 80 | 20 | 36.3 | 4.8 | 1.2 | 32.3 | — | 24.8 | 24.8 | — | 14.2 | 5.8 | — | — | 3.1 | 51.6 | — | — | 3.1 | | ,, ,, ,, |
| B | Alumina. | | | | | | | | | | | | | | | | | | | |
| 94 | 6 | 47.3 | 6.2 | 11.9 | 1.6 | — | 32.3 | 32.3 | 9.6 | 23.7 | 4.8 | 28.8 | — | — | — | — | + | 11.5 | 1,530 | Green brown solid. |
| 92 | 8 | 45.6 | 6.0 | 15.1 | 1.5 | — | 31.1 | 31.1 | 3.4 | 22.8 | 4.7 | 37.3 | — | 8.3 | — | — | + | 11.1 | | ,, ,, |
| 90 | 10 | 43.9 | 5.8 | 18.2 | 1.5 | — | 30.0 | 30.0 | — | 11.0 | 4.5 | 45.6 | — | 15.1 | — | — | — | — | | Fused. |
| 85 | 15 | 40.0 | 5.3 | 25.4 | 1.3 | — | 27.3 | 27.3 | — | — | 4.1 | 20.8 | 32.1 | — | — | — | — | — | | ,, |
| A | | | | | | | | | | | | | | | | | | | | |
| 100 | — | 54.1 | 3.5 | 1.1 | 3.3 | — | 37.4 | 37.4 | 40.9 | 13.1 | 5.3 | — | — | — | 2.6 | — | + | 18.5 | 1,450 | Black solid. |
| | Steatite F.G.X.O. | | | | | | | | | | | | | | | | | | | |
| 85 | 15 | 47.2 | 9.2 | 1.8 | 4.0 | — | 37.1 | 37.1 | 16.6 | 35.1 | 8.4 | — | — | — | 2.1 | — | + | 7.5 | 1,450 | Black solid. |
| 82 | 18 | 45.8 | 10.4 | 1.9 | 4.2 | — | 37.0 | 37.0 | 11.1 | 40.2 | 9.1 | — | — | — | 2.0 | — | + | 6.0 | | ,, ,, |
| 77 | 23 | 43.5 | 12.4 | 2.1 | 4.4 | — | 36.9 | 36.9 | 3.3 | 47.1 | 10.2 | — | — | — | 1.9 | — | + | 3.6 | | ,, ,, |
| 75 | 25 | 42.6 | 13.2 | 2.2 | 4.5 | — | 36.8 | 36.8 | — | 50.1 | 10.6 | — | — | 0.1 | 1.8 | — | — | 2.9 | | Black with dust spots. |
| 70 | 30 | 40.2 | 15.2 | 2.5 | 4.8 | — | 36.7 | 36.7 | — | 23.3 | 11.7 | — | — | 26.1 | 1.6 | — | — | 2.4 | | ,, ,, |
| A | Serpentine. | | | | | | | | | | | | | | | | | | | |
| 88 | 12 | 48.0 | 7.1 | 1.5 | 4.2 | 0.8 | 37.8 | 37.8 | 23.0 | 26.9 | 6.9 | — | — | — | 3.4 | 1.4 | + | 10.0 | 1,450 | — |
| 80 | 20 | 43.9 | 9.5 | 1.7 | 4.8 | 1.4 | 38.0 | 38.0 | 10.9 | 36.3 | 8.1 | — | — | — | 3.7 | 2.3 | + | — | | — |
| 73 | 27 | 40.3 | 11.7 | 1.9 | 5.4 | 1.8 | 38.3 | 38.3 | 0.3 | 44.5 | 9.2 | — | — | — | 4.1 | 3.2 | + | 2.3 | | — |
| 70 | 30 | 38.9 | 12.6 | 2.0 | 5.6 | 2.0 | 38.4 | 38.4 | — | 31.1 | 9.6 | — | — | 12.8 | 4.2 | 3.5 | — | 1.7 | | — |
| 65 | 35 | 36.1 | 14.2 | 2.2 | 6.1 | 2.4 | 38.5 | 38.5 | — | 4.5 | 10.3 | — | — | 37.4 | 4.5 | 4.2 | — | 1.3 | | — |

B. Bakewell and G. E. Bessey [7] have classified the quantitative methods of estimation of free lime as follows :

(1) Extraction methods using (*a*) aqueous solutions, (*b*) alcoholic solutions, (*c*) glycerol.

(2) Calorimeter methods.

(3) Other methods.

The first attempt to determine the free lime content of these clinkers followed on the work of A. A. Chadeyron and W. J. Rees,[4] who employed a water extraction method for estimating the water-soluble lime in dolomite clinkers. About 0·5 gm. of sample, ground to an impalpable powder, was accurately weighed and placed in 300 c.c. of distilled water. After standing for 24 hours, the extract was filtered off and a measured volume of N/10 HCl added. The excess acid was determined by back-titrating with N/10 NaOH, using phenol phthalein as indicator.

Longer periods of extraction were tried using the same volume of water, but little variation in the results was obtained. However, larger volumes of water and continued extraction yielded higher lime values. It was therefore concluded that some or all of the compounds present hydrolyse and that provided sufficient extraction is carried out, all the lime can probably be dissolved. Hence the water extraction method does not yield accurate free lime results unless the compounds in the clinker are unhydrolysable. The test could therefore be employed to compare the resistance to hydration of various stabilised clinkers, but not as an accurate method of determining uncombined lime.

These conclusions agree with the work of W. Lerch and R. H. Bogue [14] and B. Bakewell and G. E. Bessey.[7] It has been stated that the unhydrated compounds composing Portland cement give free lime as one of their products of hydration, due to reactions of the following type :

$$n\text{CaO.SiO}_2 + \text{Aq.} = (n-m)\text{CaO.SiO}_2.x\text{H}_2\text{O} + m\text{Ca(OH)}_2$$
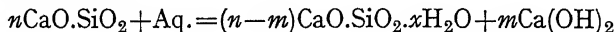
Further, W. Lerch and R. H. Bogue [15] found that these hydrated compounds are readily hydrolysed, so that extraction with water removes all the lime, provided the lime concentration in the solution is lower than that which gives the hydrolysis $p$H of the compound present.

*Extraction by Aqueous Solutions of Sugar.*—This method was developed as a result of the work of J. E. MacKenzie and J. P. Quin [16] on the compounds of calcium hydroxide with sugars. The lime forms a series of compounds with sucrose, which are readily hydrolysed to give an alkaline solution. B. Bakewell and G. E. Bessey [7] pointed out that the tendency of the calcium silicates and aluminates to hydrolyse is decreased with increasing $p$H of the solution. However, it has been shown [17] that although consistent results can be obtained with standard conditions, the results vary with time of extraction and with the concentration and volume of

sugar solution employed. Hence, the method does not give true values for the free lime content.

*Glycerol Extraction Methods.*—According to B. Bakewell and G. E. Bessey [7] the most successful means hitherto employed for the estimation of free lime is that using glycerol as the reagent for dissolving lime. There are two modifications of the original method of W. E. Emley [18]; the first is due to W. Lerch and R. H. Bogue [14] and the second to H. Rathke.[19] B. Bakewell and G. E. Bessey [7] confirmed the former method and have also found a modified form of the latter method to be satisfactory. The method used by the present authors was that of W. Lerch and R. H. Bogue.[14] Full details of the method and the precautions necessary have been described elsewhere.[7] The results obtained for various samples from group 1 are shown in Table V.

TABLE V.—COMPARISON OF CALCULATED AND DETERMINED FREE LIME CONTENTS.

| Composition of Mix. | | Percentage Free Lime. | |
| --- | --- | --- | --- |
| Percentage Dolomite B. | Percentage Stabiliser. | Calculated. | Determined. |
| 100 | — | 29·64 | 28·40 |
| 96 | 4 flint. | 8·36 | 8·26 |
| 95 | 5 steatite A.T.I. | 18·12 | 16·28 |
| 96 | 4 steatite A. | 15·64 | 16·46 |
| 92 | 8 steatite A. | 4·04 | 4·39 |
| 95 | 5 steatite F.G.X.O. | 17·41 | 18·16 |
| 90 | 10 steatite F.G.X.O. | 5·75 | 5·88 |
| 95 | 5 steatite 3B. | 14·51 | 16·40 |
| 92 | 8 olivine. | 8·89 | 8·18 |
| 90 | 10 olivine. | 5·03 | 5·09 |
| 95 | 5 serpentine. | 18·60 | 19·16 |
| 93 | 7 serpentine. | 14·37 | 14·65 |
| 90 | 10 serpentine. | 8·15 | 7·00 |
| 85 | 15 serpentine. | 0·0 | 0·0 |
| 96 | 4 bentonite. | 15·33 | 16·50 |
| 94 | 6 bentonite. | 8·36 | 7·47 |
| 95 | 5 china clay. | 10·36 | 10·60 |
| 90 | 10 ferric oxide. | 13·37 | 12·71 |
| 86 | 14 ferric oxide. | 7·39 | 7·04 |

The determined and calculated results show remarkably close agreement when the various probable errors involved in the analysis, mixing of the materials, and the free lime determination are considered. It may be easily demonstrated that errors to be expected in analysis and mixing could account for the maximum difference shown in Table V.

*Group* 2.

All the calcined mixes of group 2 (*see* Table VI) have as their constituent oxides lime, alumina, silica, iron oxide, manganese oxide, and magnesia.

The initial break in the hydration curve for dolomite–acid open-hearth slag clinkers (Fig. 2) corresponds to a composition at which there are just sufficient acidic oxides to combine with all the lime, as shown by White's test for free lime. The dusting phenomenon is also evidence for the presence of $2CaO.SiO_2$.

The various thermal equilibrium diagrams connected with this problem may be tabulated by noting the binary, ternary, quaternary, five and six-component combinations of the oxides CaO, $SiO_2$, $Al_2O_3$, FeO, MnO, MgO, and $SiO_2$. A study of the compilation of the thermal equilibrium diagrams by F. P. Hall and H. Insley [9] reveals that much of this information is not available. Further, acid open-hearth slag consists chiefly of ferrous and manganous silicates and free silica ; on heating mixtures of dolomite and slag in a gas-fired furnace the state of oxidation of the iron and manganese may be altered. An interpretation of the free lime results obtained by White's test (Table VI) is as follows : The fourth mix in the series is the first to give a negative free lime test. Assuming all the silica to react with lime to form $3CaO.SiO_2$, the $Fe_2O_3$ and $Al_2O_3$ to form $4CaO.Al_2O_3.Fe_2O_3$ and $3CaO.Al_2O_3$, and the FeO and MnO to remain unoxidised, it may be calculated that this clinker would contain free lime. Hence it is necessary to postulate that the ferrous and manganous silicates yield all their silica for combination with CaO to form $3CaO.SiO_2$ and that the FeO and MnO set free are oxidised to $Fe_2O_3$ and $MnO_2$, which then react with the remaining lime. Further, if $MnO_2$ is omitted from the calculations or $CaO.MnO_2$ postulated, the mix would contain free lime. To satisfy the free lime test it is necessary to postulate the formation of $2CaO.MnO_2$. Further evidence that such a compound is formed is to be found in the work of G. Rousseau,[20] who fired mixtures of lime and manganous salts to high temperatures and obtained $2CaO.MnO_2$.

The calculations of the constitution of some of the mixes of Table VI were carried out as follows :

*Calcined Dolomite B* (*see* group 1 and Table III, page 26).

*96 per cent. dolomite ; 4 per cent. acid open-hearth slag.*

1·93 gm. $Al_2O_3$ combine with $\dfrac{224 \times 1·93}{102} = 4·24$ gm. CaO and with $\dfrac{160 \times 1·93}{102} = 3·02$ gm. of $Fe_2O_3$ to form $4CaO.Al_2O_3.Fe_2O_3$. Thus the percentage by weight of $4CaO.Al_2O_3.Fe_2O_3$ is 9·19.

10·25 gm. $SiO_2$ combine with $\dfrac{168 \times 10·25}{60} = 28·7$ gm. CaO, to form

TABLE VI.—DATA ON DOLOMITE B–ACID OPEN-HEARTH SLAG CLINKERS FIRED TO 1,530° C, FOR 3 HOURS.

| Mix. | Dolomite, per cent. | Slag, per cent. | CaO, per cent. | $SiO_2$, per cent. | $Al_2O_3$, per cent. | $Fe_2O_3$, per cent. | MnO, per cent. | MgO, per cent. | White's Test for Free Lime. | Steam Hydration Index, per cent. | Description. |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 100 | 0 | 52·6 | 6·9 | 1·8 | 1·8 | — | 36·0 | + | 11·2 | Black solid. |
| 2 | 96 | 4 | 49·2 | 10·3 | 1·9 | 3·0 | 1·2 | 33·5 | + | 6·3 | ,,　,, |
| 3 | 94 | 6 | 47·5 | 11·8 | 2·0 | 3·6 | 1·8 | 32·3 | + | 4·8 | ,,　,, |
| 4 | 92 | 8 | 45·9 | 13·3 | 2·1 | 4·2 | 2·4 | 31·1 | — | 3·9 | ,,　,, |
| 5 | 90 | 10 | 44·4 | 14·8 | 2·1 | 4·8 | 2·9 | 30·0 | — | 3·8 | ,,　,, |
| 6 | 87 | 13 | 42·1 | 16·9 | 2·2 | 5·6 | 3·7 | 28·3 | — | 3·1 | Completely dusted. |
| 7 | 85 | 15 | 40·7 | 18·3 | 2·3 | 6·1 | 4·2 | 27·3 | — | 1·7 | ,,　,, |
| 8 | 83 | 17 | 39·3 | 19·6 | 2·3 | 6·6 | 4·7 | 26·3 | — | 1·2 | ,,　,, |

$3CaO.SiO_2$. Thus the percentage by weight of $3CaO.SiO_2$ is 38·95.

1·51 gm. $MnO_2$ combine with $\dfrac{112 \times 1·51}{87} = 1·94$ gm. CaO to form $2CaO.MnO_2$: Thus the percentage by weight of $2CaO.MnO_2$ is 3·45.

The percentage by weight of *free lime* is $49·2 - (4·24 + 28·7 + 1·94) = 14·3$.

The percentage by weight of *magnesia* as *periclase* is assumed to be 33·47.

### 94 per cent. dolomite ; 6 per cent. acid open-hearth slag.

Similar calculations to those given above indicate the constitution of this clinker to be : free lime, 6·9 per cent. ; $3CaO.SiO_2$, 44·9 per cent. ; $4CaO.Al_2O_3.Fe_2O_3$, 9·5 per cent. ; $2CaO.Fe_2O_3$, 0·8 per cent. ; $2CaO.MnO_2$, 5·0 per cent. ; MgO (periclase), 32·3 per cent.

### 92 per cent. dolomite ; 8 per cent. acid open-hearth slag.

2·06 gm. $Al_2O_3$ combine with $\dfrac{224 \times 2·06}{102} = 4·52$ gm. CaO and with $\dfrac{160 \times 2·06}{102} = 3·23$ gm. $Fe_2O_3$ to form $4CaO.Al_2O_3.Fe_2O_3$. Thus the percentage by weight of $4CaO.Al_2O_3.Fe_2O_3$ is 9·81.

$(4·19 - 3·23)$ gm. $Fe_2O_3$ combine with $\dfrac{112 \times 0·96}{160} = 0·67$ gm. CaO to form $2CaO.Fe_2O_3$. Thus the percentage by weight of $2CaO.Fe_2O_3$ is 1·63.

2·92 gm. $MnO_2$ combine with $\dfrac{112 \times 2·92}{87} = 3·76$ gm. CaO to form 6·68 gm. of $2CaO.MnO_2$.

Let $x$ be the weight of silica combined as $3CaO.SiO_2$, then $(13·34 - x)$ is combined as ${}_{,2}$ and $\dfrac{168x}{60} + \dfrac{(13·34 - x)112}{60} = 45·93$ $-(3·76 + 0·67 + 4·52)$, from which $x = 12·94$ and the percentage by weight of $3CaO.SiO_2$ is 49·17 and of $2CaO.SiO_2$ is 1·15.

The percentage by weight of *periclase* is assumed to be 31·1.

Further evidence for the validity of these calculations was obtained by a quantitative free lime determination on clinker from 96 per cent. dolomite and 4 per cent. of slag ; the free lime content was found to be 13·77 per cent., which compares satisfactorily with the calculated result of 14·3 per cent.

There are not sufficient available data to permit the calculation of the constitution of the remaining mixes of Table VI. However, the dusting of mixes 6, 7, and 8 reveals that these contain a high percentage of $2CaO.SiO_2$. Consider mix 8. Calculations based on

the assumption that FeO and MnO are oxidised to form $Fe_2O_3$ and $MnO_2$ which react as in mixes 2 to 4 show a zero content of $2CaO.SiO_2$. Hence it is probable that beyond mix 4, part or all of the FeO and MnO remain combined with silica. Examination of the $CaO-FeO-SiO_2$ [21] diagram shows that compounds of the type $CaO.FeO.SiO_2$ are to be expected. However, X-ray and petrographic evidence would be necessary before the constitution could be definitely determined.

*Group* 3.

The zirconium minerals, baddeleyite and zircon, occur fairly extensively in nature. Since these are very refractory, it was considered probable that zirconia and zirconium silicate could be employed as stabilisers for dolomite. Further, since $TiO_2$ occurs in these minerals it was decided to study the reaction between dolomite and rutile as well as those of dolomite and zirconium minerals.

All the calcined mixes of (*a*) dolomite B and zirconia, (*b*) dolomite B and synthetic zircon, (*c*) dolomite B and baddeleyite have CaO, $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $ZrO_2$, and MgO as their constituent oxides. In all three cases the initial breaks in the hydration curves (Fig. 4) corresponded to the composition at which all the lime had just attained the combined state.

F. P. Hall and H. Insley,[9] list only two of the appropriate thermal equilibrium diagrams dealing with $ZrO_2$, namely, the binary diagrams $CaO-ZrO_2$ and $ZrO_2-SiO_2$. The very refractory compound $CaO.ZrO_2$ is the only one to be found in the diagram $CaO-ZrO_2$. H. Wartenberg and H. Wert [22] have reported the occurrence of $MgO.ZrO_2$ in the $MgO-ZrO_2$ system. Their work has not been confirmed by N. A. Shirnova [23] nor is the stability of $MgO.ZrO_2$ in the presence of lime known. Although all the thermal equilibrium data were not available it was found possible to calculate the constitution on certain assumptions :

(*a*) As for group 1, the available data indicated that magnesia would appear as periclase in all the calcined mixes of dolomite B–zirconia and dolomite B–synthetic zircon respectively.

(*b*) Although the five-component system $CaO-SiO_2-Al_2O_3-Fe_2O_3-ZrO_2$ has not yet been investigated, the compositions of these mixes are to be found in the $CaO-2CaO.SiO_2-5CaO.3Al_2O_3-4CaO.Al_2O_3.Fe_2O_3-CaO.ZrO_2$ portion of the diagram. On the assumption that $CaO.ZrO_2$ is the only compound of $ZrO_2$ formed in this part of the diagram, it was found possible to calculate the constitution in a similar manner to that employed for group 1.

The calcined mixes of dolomite B–rutile have as their constituent oxides CaO, $SiO_2$, $Al_2O_3$, $Fe_2O_3$, $TiO_2$, and MgO. The various appropriate thermal equilibrium diagrams have been noted and the available data have been studied. Unfortunately, as found by referring to the compilation by F. P. Hall and H. Insley,[9] much of the information is not available, but melting diagrams of CaO and $TiO_2$ [24] have been investigated indicating that three compounds of CaO and $TiO_2$ are possible, namely, $3CaO.TiO_2$, $2CaO.TiO_2$, and $CaO.TiO_2$. As for the previous series of group 3, it was found possible to calculate the constitution making two assumptions.

(a) The available data indicated that magnesia would crystallise as periclase in all the mixes. This was the first assumption.

(b) The compositions of the mixes are to be found in the $CaO–2CaO.SiO_2–4CaO.Al_2O_3.Fe_2O_3–5CaO.3Al_2O_3–TiO_2$ portion of the $CaO–SiO_2–Al_2O_3–Fe_2O_3–TiO_2$ diagram. Various calculations were made postulating various $TiO_2$ compounds of CaO, but the only set of calculations which yielded free lime contents agreeing with the results of White's test and the initial break in the hydration curve (Fig. 4) was that which postulated that all the $TiO_2$ present reacted to form $2CaO.TiO_2$. This was the second assumption.

All the calcined mixes of the dolomite B–zircon series have as their constituent oxides $CaO–SiO_2–Al_2O_3–Fe_2O_3–TiO_2–ZrO_2–MgO$. As for the previous series in group 3, it was possible to calculate the constitution, making the following assumptions.

(a) That magnesia would crystallise out as periclase.

(b) That the titania would combine with lime to form $2CaO.TiO_2$ and the zirconia to form $CaO.ZrO_2$. The composition of the mixes lie in the $CaO–2CaO.SiO_2–4CaO.Al_2O_3.Fe_2O_3–5CaO.3Al_2O_3–CaO.ZrO_2–2CaO.TiO_2$ portion of the six-component diagram $CaO–SiO_2–Al_2O_3–Fe_2O_3–TiO_2–ZrO_2$.

It was found on making calculations postulating various compounds that the only set of calculations yielding free lime results concordant with those obtained by White's free lime test and the initial breaks in the hydration curves (Fig. 4) was that in which all the $TiO_2$ formed $2CaO.TiO_2$ and the $ZrO_2$ formed $CaO.ZrO_2$.

The following are typical examples of the calculations of the constitution of mixes of Table VII (see page 38).

*95 per cent. dolomite B ; 5 per cent. natural zircon.*

1·67 gm. $Fe_2O_3$ combine with $\dfrac{224 \times 1\cdot 67}{160} = 2\cdot 34$ gm. CaO and

with $\dfrac{102 \times 1 \cdot 67}{160} = 1 \cdot 06$ gm. $Al_2O_3$. Thus the percentage by weight of $4CaO.Al_2O_3.Fe_2O_3 = 5 \cdot 07$.

$4 \cdot 96$ gm. $ZrO_2$ combine with $\dfrac{56 \times 4 \cdot 96}{122 \cdot 6} = 2 \cdot 27$ gm. CaO. Thus the percentage by weight of $CaO.ZrO_2 = 7 \cdot 23$. $0 \cdot 78$ gm. $TiO_2$ combine with $\dfrac{112 \times 0 \cdot 78}{80} = 1 \cdot 09$ gm. CaO. Thus the percentage by weight of $2CaO.TiO_2 = 1 \cdot 87$.

$(1 \cdot 74 - 1 \cdot 06)$ gm. $Al_2O_3$ combine with $\dfrac{168 \times 0 \cdot 68}{102} = 1 \cdot 12$ gm. CaO. Thus the percentage by weight of $3CaO.Al_2O_3 = 1 \cdot 80$.

$9 \cdot 17$ gm. $SiO_2$ combine with $\dfrac{168 \times 9 \cdot 17}{60} = 25 \cdot 68$ gm. CaO. Thus the percentage by weight of $3CaO.SiO_2 = 34 \cdot 85$. The percentage by weight of *free lime* is $48 \cdot 13 - (2 \cdot 34 + 2 \cdot 27 + 1 \cdot 09 + 1 \cdot 12 + 25 \cdot 68) = 15 \cdot 63$. The percentage by weight of *periclase* $= 32 \cdot 90$.


*85 per cent. dolomite B ; 15 per cent. synthetic zircon.*

$1 \cdot 34$ gm. $Fe_2O_3$ combine with $\dfrac{224 \times 1 \cdot 34}{160} = 1 \cdot 88$ gm. CaO and with $\dfrac{102 \times 1 \cdot 34}{160} = 0 \cdot 85$ gm. $Al_2O_3$. Thus the percentage by weight of $4CaO.Al_2O_3.Fe_2O_3 = 4 \cdot 07$.

$(1 \cdot 35 - 0 \cdot 85)$ gm. $Al_2O_3$ combine with $\dfrac{168 \times 0 \cdot 5}{102} = 0 \cdot 82$ gm. CaO. Thus the percentage by weight of $3CaO.Al_2O_3 = 1 \cdot 32$. $16 \cdot 19$ gm. $ZrO_2$ combine with $\dfrac{56 \times 16 \cdot 19}{122 \cdot 6} = 7 \cdot 4$ gm. CaO. Thus the percentage by weight of $CaO.ZrO_2 = 23 \cdot 59$.

The silica is assumed to combine with all the remaining lime to form $3CaO.SiO_2$ and $2CaO.SiO_2$. The percentage of lime available is $39 \cdot 99 - (7 \cdot 4 + 0 \cdot 72 + 1 \cdot 88) = 29 \cdot 89$. Let $x$ be percentage of silica combined as $3CaO.SiO_2$, then $\dfrac{168x}{60} + \dfrac{(13 \cdot 2 - x)}{60} \times 112 = 29 \cdot 89$, whence $x = 5 \cdot 63$ and the percentage by weight of $3CaO.SiO_2 = 21 \cdot 39$, and the percentage by weight of $2CaO.SiO_2 = 21 \cdot 70$. The percentage by weight of *periclase* $= 27 \cdot 30$.

The calculated constitutions of the fired mixes of group 3 are given in Table VII.

Confirmatory evidence for these calculations was obtained by quantitative free lime determinations shown in Table VIII.

TABLE VII.—DATA ON THE CONSTITUTION OF DOLOMITE CLINKERS.

| Dolomite, per cent. | Stabiliser, per cent. | Ultimate Analysis of Clinker, per cent. | | | | | | | Calculated Mineralogical Composition (Weight, per cent.). | | | | | | | | | White's Free Lime Test. | Steam Hydration Index, per cent. | Firing Treatment, 3 hours at: |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CaO$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $ZrO_2$ | $TiO_2$ | $MgO$ | Periclase, $MgO$ | Free Lime. | $3CaO.SiO_2$ | $4CaO.Al_2O_3.Fe_2O_3$ | $3CaO.Al_2O_3$ | $2CaO.SiO_2$ | $5CaO.3Al_2O_3$ | $CaO.ZrO_2$ | $2CaO.TiO_2$ | | | |
| B 100 | — | 52·6 | 6·9 | 1·8 | 1·8 | — | — | 36·0 | 36·0 | 29·6 | 26·4 | 5·4 | 1·7 | — | — | — | — | + | 11·2 | 1,530° C. |
| 80 | Zirconia. 20 | 36·3 | 4·8 | 1·2 | 1·2 | 31·0 | — | 24·8 | 24·8 | 6·4 | 18·2 | 3·7 | 1·2 | — | — | 45·1 | — | + | 4·9 | 1,530° C. |
| 77 | 23 | 34·3 | 4·5 | 1·2 | 1·2 | 35·0 | — | 23·4 | 23·4 | 3·3 | 17·2 | 3·5 | 1·1 | — | — | 50·9 | — | + | 3·6 | |
| 75 | 25 | 32·9 | 4·3 | 1·1 | 1·1 | 37·5 | — | 22·5 | 22·5 | 1·4 | 16·5 | 3·3 | 1·1 | — | — | 54·6 | — | + | 2·9 | |
| 73 | 27 | 31·6 | 4·2 | 1·1 | 1·1 | 40·0 | — | 21·6 | 21·6 | — | 14·1 | 3·2 | 1·0 | 1·3 | — | 58·2 | — | — | 2·6 | |
| B 95 | Synthetic Zircon. 5 | 48·1 | 9·2 | 1·6 | 1·6 | 5·8 | — | 32·9 | 32·9 | 16·5 | 34·9 | 4·9 | 1·6 | — | — | 8·5 | — | + | 8·1 | 1,530° C. |
| 93 | 7 | 46·4 | 10·0 | 1·6 | 1·6 | 8·0 | — | 31·7 | 31·7 | 11·5 | 38·2 | 4·7 | 1·5 | — | — | 11·7 | — | + | 4·6 | |
| 90 | 10 | 43·9 | 11·3 | 1·5 | 1·5 | 11·2 | — | 30·0 | 30·0 | — | 42·8 | 4·5 | 1·5 | — | — | 16·3 | — | + | 3·3 | |
| 88 | 12 | 42·3 | 12·1 | 1·4 | 1·4 | 13·2 | — | 28·9 | 28·9 | — | 44·5 | 4·3 | 1·4 | 1·0 | — | 19·3 | — | — | 4·0 | |
| 85 | 15 | 40·0 | 13·2 | 1·4 | 1·3 | 16·2 | — | 27·3 | 27·3 | — | 21·4 | 4·1 | 1·3 | 21·7 | — | 23·6 | — | — | 4·0 | |

| B | Sample | | | | | | | | | | | | | | | | | | Temp. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Natural Zircon. | | | | | | | | | | | | | | | | | | |
| 95 | 5 | 48·1 | 9·2 | 1·7 | 1·7 | 5·0 | 0·8 | 32·9 | 32·9 | 15·6 | 34·9 | 5·1 | 1·8 | — | — | 7·2 | 1·9 | + | 7·3 | 1,530° C. |
| 90 | 10 | 43·9 | 11·2 | 1·7 | 1·6 | 9·6 | 1·3 | 30·0 | 30·0 | 3·0 | 42·6 | 4·8 | 1·8 | — | — | 13·9 | 3·1 | + | 3·0 | |
| 88 | 12 | 42·3 | 12·0 | 1·7 | 1·6 | 11·3 | 1·5 | 28·9 | 28·9 | — | 38·0 | 4·7 | 1·9 | — | 5·8 | 16·4 | 3·6 | - | 3·1 | |
| 85 | 15 | 40·0 | 13·1 | 1·7 | 1·5 | 13·8 | 1·8 | 27·3 | 27·3 | — | 14·0 | 4·6 | 1·9 | — | 27·1 | 20·1 | 4·3 | - | 2·7 | |
| 83 | 17 | 38·5 | 13·9 | 1·7 | 1·5 | 15·5 | 2·0 | 26·3 | 26·3 | — | — | 4·5 | 0·3 | 1·1 | 39·8 | 22·5 | 4·7 | - | 2·8 | |
| | Baddeleyite. | | | | | | | | | | | | | | | | | | |
| 95 | 5 | 48·3 | 6·9 | 1·9 | 2·2 | 6·6 | 0·2 | 32·8 | 32·8 | 21·9 | 26·1 | 6·8 | 1·2 | — | — | 9·6 | 0·5 | + | 9·1 | 1,530° C |
| 90 | 10 | 44·1 | 6·8 | 2·0 | 2·7 | 12·8 | 0·5 | 30·2 | 30·2 | 14·2 | 26·0 | 8·2 | 0·7 | — | — | 18·6 | 1·3 | + | 7·3 | |
| 85 | 15 | 40·1 | 6·8 | 2·1 | 3·1 | 18·5 | 0·7 | 27·5 | 27·5 | 7·6 | 25·8 | 9·4 | 0·2 | — | — | 26·9 | 1·6 | + | 5·4 | |
| 83 | 17 | 38·8 | 6·8 | 2·1 | 3·3 | 20·7 | 0·7 | 26·5 | 26·5 | 4·6 | 25·8 | 9·9 | 0·2 | — | — | 30·2 | 1·7 | + | 4·6 | |
| 80 | 20 | 36·6 | 6·7 | 2·2 | 3·5 | 23·9 | 0·8 | 25·0 | 25·0 | 1·0 | 25·6 | 10·2 | — | — | — | 34·8 | 1·9 | - | 3·8 | |
| 77 | 23 | 34·6 | 6·7 | 2·2 | 3·7 | 26·9 | 0·8 | 23·6 | 23·6 | — | 14·6 | 10·4 | — | — | 8·3 | 39·2 | 2·0 | - | 3·7 | |
| 75 | 25 | 33·3 | 6·7 | 2·3 | 3·9 | 28·9 | 0·9 | 22·7 | 22·7 | — | 5·0 | 10·7 | — | — | 15·4 | 42·1 | 2·1 | - | 3·4 | |
| | Rutile. | | | | | | | | | | | | | | | | | | |
| 95 | 5 | 48·1 | 6·5 | 1·6 | 1·8 | — | 8·9 | 33·0 | 33·0 | 14·4 | 24·5 | 5·5 | 1·3 | — | — | — | 21·2 | + | 9·6 | 1,570° C. |
| 93 | 7 | 46·4 | 6·1 | 1·6 | 1·8 | — | 12·1 | 31·7 | 31·7 | 9·1 | 23·3 | 5·5 | 1·1 | — | — | — | 21·1 | + | 7·8 | |
| 90 | 10 | 43·9 | 6·0 | 1·5 | 1·9 | — | 16·2 | 30·0 | 30·0 | 1·4 | 22·8 | 5·6 | 0·8 | — | — | — | 38·8 | + | 5·6 | |
| 88 | 12 | 42·3 | 5·8 | 1·4 | 1·9 | — | 19·1 | 28·9 | 28·9 | — | 7·2 | 5·7 | 0·6 | — | 11·2 | — | 45·8 | - | 4·2 | |

TABLE VIII.—COMPARISON OF CALCULATED AND DETERMINED FREE
LIME CONTENTS OF VARIOUS DOLOMITE CLINKERS.

| Percentage Dolomite B. | Percentage Stabiliser. | Percentage Free Lime. | |
| --- | --- | --- | --- |
| | | Calculated. | Determined. |
| 93 | 7 synthetic zircon. | 11·50 | 11·66 |
| 93 | 7 rutile. | 9·05 | 8·98 |
| 95 | 5 zircon. | 15·64 | 15·86 |
| 80 | 20 zirconia. | 6·39 | 6·48 |

Further confirmation was obtained by the dusting of the mix containing initially 17 per cent. zircon (Table VII), which has about 40 per cent. $2CaO.SiO_2$; on the other hand, no dusting occurred in the dolomite B–synthetic zircon series, but this is in agreement with the calculated $2CaO.SiO_2$ contents, which do not exceed 22 per cent.

*Group 4.*

All the calcined mixes of group 4 have as their constituent oxides lime, silica, alumina, ferric oxide, chromic oxide, and magnesia. The various appropriate thermal equilibrium diagrams were tabulated by noting the various two, three, four, five, and six-component combinations of these six oxides. The available data were studied, but unfortunately many of the $Cr_2O_3$ diagrams have not yet been investigated. However, W. Hugill, A. Watts, and J. Vyse [25] found that a calcium chromite $(2CaO.Cr_2O_3)$ was formed on calcination of mixtures containing chromite, alumina, magnesia, and calcium fluoride.

The compositions of the majority of the mixes are to be found in the $CaO–2CaO.SiO_2–4CaO.Al_2O_3.Fe_2O_3–5CaO.3Al_2O_3–2CaO.Cr_2O_3$ portion of the $CaO–SiO_2–Al_2O_3–Fe_2O_3–Cr_2O_3$ diagram; the dolomite B–synthetic chromite compositions, however, lie in the $CaO–2CaO.SiO_2–2CaO.Fe_2O_3–4CaO.Al_2O_3.Fe_2O_3–2CaO.Cr_2O_3$ portion of the diagram.

Various calculations were made postulating various $Cr_2O_3$ compounds of CaO, but the only set of calculations which yielded free lime contents concordant with White's test for free lime and the initial breaks in the hydration curves (Fig. 5) was that postulating the formation of $2CaO.Cr_2O_3$. The calculations were carried out on this assumption and on that of the magnesia crystallising as periclase.

The constitutions of the various series of group 4 thus obtained are given in Table IX (*see* pages 42–43).

Confirmation of these calculations was obtained by quantitative free lime analysis of the clinkers 90 per cent. dolomite B–10 per

cent. chromite A and 85 per cent. dolomite B–15 per cent. chromic oxide. The theoretical free lime contents were 12·5 and 4·8 per cent. respectively, which compared satisfactorily with the experimental value of 13·7 and 5 per cent.

TECHNICAL APPLICATIONS.

*The Constitution of Dolomite Bricks.*

As an illustration of the application of the foregoing principles to commercial products the constitution of a dolomite brick has been worked out in the same way as that used for the dolomite sinters of group 1. The results are given in Table X. Experimental data on the free lime content and steam hydration index are also included, which confirm the results of the calculated constitution.

TABLE X.—CALCULATED CONSTITUTION OF A COMMERCIAL
DOLOMITE BRICK.

|  | *Per cent.* |
|---|---|
| Analysis : | |
| SiO$_2$ | 15·92 |
| TiO$_2$ | 0·14 |
| Al$_2$O$_3$ | 1·02 |
| Fe$_2$O$_3$ | 3·62 |
| CaO | 37·80 |
| MgO | 40·68 |
| Loss on ignition | — |
| | |
| Calculated constitution : | |
| Periclase, MgO | 40·7 |
| Free lime, CaO | Nil. |
| 3CaO.SiO$_2$ | 18·1 |
| 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ | 4·9 |
| 3CaO.Al$_2$O$_3$ | Nil. |
| 2CaO.SiO$_2$ | 32·0 |
| 2CaO.Fe$_2$O$_3$ | 3·4 |
| White's test for free lime | Negative. |
| Free lime determination | Nil. |
| | |
| Steam hydration index | 2·87 |

Further confirmation of these conclusions is to be found in the work of A. A. Grebenjuk,[26] who found that on addition of silica to dolomite the following lime minerals are formed : 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, 2CaO.Fe$_2$O$_3$ or 3CaO.Al$_2$O$_3$, and that only the remaining lime combines with the silica to form 3CaO.SiO$_2$. To obtain dead-burned clinker containing no free lime from dolomite, A. A. Grebenjuk [26] calculated from the composition of the dolomite that 8·53 per cent. SiO$_2$ was required. This dolomite had the

TABLE IX.—DATA ON THE CONSTITUTION OF CHROME-DOLOMITE CLINKERS FIRED TO 1,530° C. FOR THREE HOURS.

| Dolomite, per cent. | Stabiliser, per cent. | Ultimate Analysis of Clinker, per cent. | | | | | | Calculated Mineralogical Composition (Weight, per cent.) | | | | | | | | White's Free Lime Test. | Steam Hydration Index, per cent. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $CaO$ | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $Cr_2O_3$ | $MgO$ | Periclase, $MgO$ | Free Lime | $3CaO.SiO_2$ | $4CaO.Al_2O_3.Fe_2O_3$ | $3CaO.Al_2O_3$ | $2CaO.SiO_2$ | $2CaO.Fe_2O_3$ | $2CaO.Cr_2O_3$ | | |
| B 100 | — | 52·6 | 6·9 | 1·8 | 1·8 | — | 36·0 | 36·0 | 29·6 | 26·4 | 5·4 | 1·7 | — | — | — | + | 11·2 |
| B | Chromic-Oxide. | | | | | | | | | | | | | | | | |
| 95 | 5 | 48·1 | 6·3 | 1·6 | 1·6 | 8·7 | 32·9 | 32·9 | 20·8 | 24·1 | 4·9 | 1·6 | — | — | 15·0 | ++++ | 3·8 |
| 90 | 10 | 43·9 | 5·8 | 1·5 | 1·5 | 16·7 | 30·0 | 30·0 | 12·5 | 22·0 | 4·5 | 1·4 | — | — | 28·9 | +++ | — |
| 85 | 15 | 40·0 | 5·3 | 1·3 | 1·3 | 24·1 | 27·3 | 27·3 | 4·8 | 20·0 | 4·1 | 1·3 | — | — | 41·9 | +++ | 0·7 |
| 83 | 17 | 38·5 | 5·1 | 1·3 | 1·3 | 26·9 | 26·3 | 26·3 | 1·9 | 19·3 | 3·9 | 1·3 | — | — | 46·8 | + | 0·5 |
| 80 | 20 | 36·3 | 4·8 | 1·2 | 1·2 | 31·0 | 24·8 | 24·8 | — | 8·5 | 3·7 | 1·2 | 7·3 | — | 53·9 | — | 0·2 |
| B | Synthetic Chromite. | | | | | | | | | | | | | | | | |
| 95 | 5 | 48·0 | 6·3 | 1·6 | 4·7 | 5·9 | 32·8 | 32·8 | 20·9 | 24·0 | 7·7 | — | — | 3·7 | 10·3 | ++++ | 5·1 |
| 90 | 10 | 43·7 | 5·8 | 1·5 | 7·4 | 11·2 | 29·8 | 29·8 | 12·7 | 21·9 | 7·1 | — | — | 8·6 | 19·5 | +++ | 3·4 |
| 85 | 15 | 39·7 | 5·2 | 1·3 | 9·9 | 16·2 | 27·1 | 27·1 | 4·7 | 19·9 | 6·4 | — | — | 13·2 | 28·2 | +++ | 1·0 |
| 83 | 17 | 38·1 | 5·0 | 1·3 | 10·8 | 18·1 | 26·1 | 26·1 | 1·8 | 19·1 | 6·1 | — | — | 15·0 | 31·5 | + | 0·5 |
| 80 | 20 | 35·9 | 4·7 | 1·2 | 12·2 | 20·8 | 24·6 | 24·6 | — | 7·6 | 5·8 | — | 7·8 | 17·4 | 36·2 | — | 0·4 |

| B | Chromite A | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 95 | 5 | 48·3 | 7·0 | 2·6 | 2·9 | 3·6 | 34·8 | 34·8 | 20·8 | 26·6 | 8·7 | 2·0 | — | — | 6·3 | + | 7·5 |
| 90 | 10 | 44·3 | 7·1 | 3·3 | 3·9 | 7·0 | 33·7 | 33·7 | 12·5 | 26·8 | 11·8 | 2·2 | — | — | 12·1 | + | 5·2 |
| 85 | 15 | 40·6 | 7·1 | 4·0 | 4·9 | 10·1 | 32·8 | 32·8 | 4·9 | 27·1 | 14·8 | 2·4 | — | — | 17·6 | + | 1·2 |
| 83 | 17 | 39·0 | 7·2 | 4·3 | 5·2 | 11·4 | 32·5 | 32·5 | 1·7 | 27·3 | 15·8 | 2·5 | — | — | 19·7 | + | 0·8 |
| 80 | 20 | 37·0 | 7·2 | 4·7 | 5·8 | 13·1 | 31·9 | 31·9 | — | 17·0 | 17·5 | 2·7 | 7·8 | — | 22·8 | − | 1·5 |

| B | Chromite B | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 95 | 5 | 48·3 | 7·3 | 2·7 | 3·1 | 2·8 | 34·9 | 34·9 | 20·3 | 27·7 | 9·5 | 1·9 | — | — | 4·9 | + | 7·0 |
| 90 | 10 | 44·3 | 7·6 | 3·6 | 4·4 | 5·4 | 33·9 | 33·9 | 11·9 | 28·7 | 13·3 | 2·1 | — | — | 9·2 | + | — |
| 85 | 15 | 40·5 | 7·9 | 4·4 | 5·5 | 7·9 | 32·9 | 32·9 | 3·4 | 29·9 | 16·9 | 2·3 | — | — | 13·7 | + | 2·6 |
| 83 | 17 | 39·0 | 7·9 | 4·7 | 6·0 | 8·8 | 32·6 | 32·6 | 0·4 | 30·1 | 18·2 | 2·4 | — | — | 15·3 | + | 1·5 |
| 80 | 20 | 36·8 | 8·1 | 5·2 | 6·6 | 10·1 | 31·9 | 31·9 | — | 13·5 | 20·2 | 2·5 | 13·1 | — | 17·6 | − | 0·8 |

following composition :  $SiO_2$,  0·56 per cent. ;  $Al_2O_3$, 0·68 per
cent. ;  $Fe_2O_3$, 1·60 per cent. ;  MgO, 21·82 per cent. ;  CaO, 29·33
per cent. ;  MnO, 0·20 per cent. ; loss on ignition, 45·60 per cent.

In this case the proportion of the minerals to be expected
in the clinker would be as follows :  $3CaO.SiO_2$, 58·65 per cent. ;
MgO (periclase), 34·36 per cent. ;  $2CaO.Fe_2O_3$, 1·38 per cent. ;
$4CaO.Al_2O_3.Fe_2O_3$, 5·16 per cent., and $2MnO.SiO_2$, 0·44 per cent.
A. A. Grebenjuk [26] experimented with various silica–dolomite mixes,
verifying the calculated composition petrographically.

## GENERAL PROPERTIES.

The various properties of the clinkers, such as hydration
resistance, hydraulic properties, refractoriness, behaviour during
manufacture of bricks, behaviour of bricks in practice, etc., may
now be systematically correlated with the mineral constitution.  A
detailed knowledge of the properties of the various minerals is
therefore desirable.  This will be thoroughly treated in a later
publication, but a brief discussion will be introduced here.

A. A. Grebenjuk [26] found that the calcined dolomite–silica
mixture with the best refractory properties consisted of 57 per
cent. $3CaO.SiO_2$ and 35 per cent. periclase, bonded with 8 per cent.
$4CaO.Al_2O_3.Fe_2O_3$. This material possessed valuable hydraulic
properties. The clinker when moistened and pressed under a load
of 300 kg. per sq. cm. into small bricks bound hydraulically and
after 5 days had a cold crushing strength of 76 kg. per sq. cm.
Bricks pressed from clinker with a free lime content up to 6 per cent.
disintegrated on drying.  It was possible, however, to produce
useful bricks from clinker containing up to 2 per cent. free lime
after having stored the mix for 1 day.

Hydration results for group 1 show that there is little difference
in the hydration resistance of the various clinkers for the composi-
tions at which all the lime is just combined, excepting those with a
high alumina content.  $3CaO.Al_2O_3$ is very hydraulic ;  clinkers
containing appreciable amounts of this mineral have a high hydration
tendency.  For example, in the dolomite–alumina series the
hydration tendency does not decrease although the free lime
content decreases to zero (see Table IV).  Examination of the
appropriate thermal equilibrium diagrams reveals that $Al_2O_3$ has a
severe fluxing action on dolomite ;  $3CaO.Al_2O_3$ and $5CaO.3Al_2O_3$
have fairly low melting-points and form a very low melting eutectic.
Hence it may be concluded that minerals rich in alumina are
undesirable for the production of stabilised dolomite clinker.

The properties of the various minerals present in the clinkers
from which bricks are produced may yield some clue as to the
probable behaviour of the bricks on the heating and cooling to which
these bricks are subjected in practice.  F. M. Lea and T. W.
Parker [13] found that $3CaO.SiO_2$ was unstable below 1,300° C. and

above 1,900° C.   The rate of decomposition below 1,300° C. was very slow, but on prolonged heating at about 1,250° C., $3CaO.SiO_2$ decomposed into $CaO$ and $2CaO.SiO_2$.   In steel furnace practice part of the brick will be subject to prolonged heating at 1,200° C., hence when the $3CaO.SiO_2$ content is high, failure may occur due to the decomposition of $3CaO.SiO_2$ and subsequent hydration of the free lime formed.    A. A. Grebenjuk [26] has stated that dolomite bricks containing $2CaO.SiO_2$ are unstable and that in the raw mixture the excess of silica should not exceed the calculated amount required to combine with all the lime to form $3CaO.SiO_2$ by more than 1 per cent.   It may be calculated that by increasing the silica addition to the dolomite used by A. A. Grebenjuk,[26] from 8·53 to 9·53 per cent., the constitution of the calcined mix would be : periclase, 33·6 per cent. ; $3CaO.SiO_2$, 42·83 per cent. ; $2CaO.SiO_2$, 16·51 per cent. ; $2CaO.Fe_2O_3$, 1·38 per cent. ; $4CaO.Al_2O_3.Fe_2O_3$, 5·01 per cent.

At 675° C. $2CaO.SiO_2$ undergoes a $\beta \rightarrow \gamma$ inversion which is accompanied by a 10 per cent. expansion.[10]   Dolomite clinkers with a high content of $2CaO.SiO_2$ on cooling from above 675° C. disintegrated to dust.   Examination of the series of group 1 shows that complete dusting sets in when the $2CaO.SiO_2$ content exceeds 40 per cent.   Even with low $2CaO.SiO_2$ contents isolated dust spots are liable to occur.   Further, although there may not be sufficient $2CaO.SiO_2$ in a dolomite brick to cause dusting, sudden contraction and expansion in passing through the $\beta \rightarrow \gamma$ inversion point will produce cracking.

A comparison of the efficiency of the various stabilisers is given in Table XI.

It is evident that a much greater accuracy is required in the preparation of the raw mix for dolomite–flint than for, say, dolomite–steatite F.G.X.O.   A given error in the mix will produce a greater change in the constitution of the former clinker.   That is, proceeding down Table XI, the accuracy required in preparing the mix decreases.

Clinkers prepared from dolomite–zirconia minerals compared favourably with those of groups 1 and 2 with regard to hydration resistance and refractoriness.   The high refractoriness was due to the high content of $3CaO.SiO_2$ (1,900° C.) and $CaO.ZrO_2$ (over 2,000° C.).   Probably dolomite–baddeleyite clinkers would have the highest refractoriness, but a detailed examination of the properties is now being undertaken.

The dolomite–chromite clinkers had the highest resistance to hydration of all the clinkers produced in this work.   Further, such clinkers have been found to be very refractory and free from danger of dusting, since the $2CaO.SiO_2$ content is very low.   Such stabilised dolomite bricks therefore offer some advantages.

TABLE XI.—RELATIVE EFFECTIVENESS OF DIFFERENT MATERIALS AS STABILISERS FOR DOLOMITE B.

| Stabiliser. | Minimum per cent. (Weight) Stabiliser required for Complete Combination with Lime. | Hydration Index, per cent. |
|---|---|---|
| Flint | 5·6 | 3·2 |
| China clay | 7·8 | 4·2 |
| Open-hearth slag | 7·8 | 3·9 |
| Bentonite | 8·5 | 3·5 |
| Alumina .. | 9·0 | 11·0 |
| Steatite A | 9·6 | 3·5 |
| Steatite 3B | 10·2 | 4·7 |
| Rutile | 10·5 | 5·0 |
| Zircon | 11·0 | 3·0 |
| Synthetic zircon | 11·7 | 3·4 |
| Olivine | 12·0 | 3·4 |
| Steatite F.G.X.O. | 12·5 | 3·1 |
| Steatite A.T.I. .. | 13·2 | 3·1 |
| Serpentine | 14·0 | 1·5 |
| Chromite B | 17·3 | 1·5 |
| Chromite A | 18·0 | 1·0 |
| Synthetic chromite | 18·0 | 0·4 |
| Chromic oxide .. | 18·0 | 0·4 |
| Ferric oxide | 19·0 | 3·0 |
| Baddeleyite | 21·8 | 3·8 |
| Zirconia .. | 26·4 | 2·7 |

REFERENCES.

1. A. Wasum, *Verhandlungen des Vereins zur Beförderung des Gewerbleisses* **63**, 104, 1884.
   A. Rollanson, *Pat. J.*, No. 1524, 1918.
   H. Schurecht, *J. Amer. Ceram. Soc.*, **4**, 126, 1921 ; **6**, 278, 1923.
   J. T. Robson and J. R. Withrow, *ibid.*, **7**, 61, 1924 ; **7**, 141, 1924.
   W. C. Hansen, *ibid.*, **11**, 68, 1928.
   S. Nagai and K. Akiyama, *J. Soc. Chem. Ind.* (Japan), **35**, 65, 1932.
   S. Kondo and M. Higuchi, *J. Jap. Ceram. Soc.*, **43**, 273, 1935.
   A. V. Tereschenko and O. M. Margulis, *Zitein Tesco*, No. 2268, 1936.
   F. E. Lathe and H. P. Pitt, *Chem. Eng. Congress*, World Power Conference, B1, 19, 1936.
   P. P. Budnikoff, K. F. Mukhin, and D. A. Nierenstein, *Ukrain. Khem. Zhur*, **13**, 115, 1938.
   H. Schwiete and H. Strassen, *Zement*, **25**, 843, 861, 879, 1936.
   D. A. Nierenstein, *Ogneupory*, **6**, 1494, 1572, 1938,
   A. V. Tereschenko and O. M. Margulis, *Ukrain. Nauch-Issledovatel Inst. Ogneup. Kislotoup.*, **44**, 44, 1938.
2. J. Lumsden, " Magnesium, Magnesite, Dolomite," Imperial Institute Mineral Resources Dept., London, 1939.
3. J. T. Robson and J. R. Withrow, *J. Amer. Ceram. Soc.*, **7**, 61, 141, 1924.
4. A. A. Chadeyron and W. J. Rees, *Bull. B.R.R.A.*, **47**, 26, 1938.
5. A. H. White, *Ind. Eng. Chem.*, **1**, 5, 1909.
6. W. C. Reibling and F. D. Reyes, *Philippine J. Sci.*, **5**, 367, 1910.

7. B. Bakewell and G. E. Bessey, *D.S.I.R. Building Research Spec. Rept.*, No. 17, 13, 1931.
8. A. A. Klein and A. J. Philips, *U.S. Bur. Stand. Tech. Paper No.* 43, 1914 ; G. A. Rankin and F. E. Wright, *Amer. J. Sci.*, **39**, 1, 1915.
9. F. P. Hall and H. Insley, *J. Amer. Ceram. Soc.*, **16**, 459, 1933 ; **21**, 113, 1938.
10. G. A. Rankin and F. E. Wright, *Amer. J. Sci.*, **39**, 1, 1915.
11. W. C. Hansen, L. T. Brownmiller, and R. H. Bogue, *J. Amer. Chem. Soc.*, **50**, 396, 1928.
12. W. C. Hansen and R. H. Bogue, *ibid.*, **48**, 1261, 1926.
13. F. M. Lea and T. W. Parker, *Phil. Trans. Roy. Soc.*, **234**, 1, 1934.
14. W. Lerch and R. H. Bogue, *Ind. Eng. Chem.*, **18**, 739, 1926.
15. W. Lerch and R. H. Bogue, *J. Phys. Chem.*, **31**, 627, 1927.
16. J. E. MacKenzie and J. P. Quin, *J. Chem. Soc.*, **128**, 951, 1929.
17. F. L. Brady and F. J. McConnell, *Building Research Tech. Paper*, No. 4, London, 1926.
18. W. E. Emley, *Trans. Amer. Ceram. Soc.*, **17**, 720, 1915.
19. H. Rathke, *Tonind. Ztg.*, **52**, 1318, 1928.
20. J. W. Mellor, "A Comprehensive Treatise on Theoretical and Inorganic Chemistry," Longmans, Green & Co., London, **12**, 277, 1932.
21. N. L. Bowen, J. F. Schairer, and E. Posnjak, *Amer. J. Sci.*, **26**, 193, 1933.
22. H. Wartenberg and H. Wert, *Zeit. allgem. anorg. Chem.*, **190**, 179, 1930.
23. N. A. Shirnova, *J. Prikl. Chim.*, **12**, 1, 286, 1939.
24. H. J. Reusch and H. Wartenberg, *Heraeus-Vacuumschmelze Anniv. Vol.*, Hanau, 350, 1933.
25. W. Hugill, A. Watts, and J. Vyse, *Bull. B.R.R.A.*, **51**, 5, 1939.
26. A. A. Grebenjuk, *Ukrain. Inst. Ogneup. Kislotoup.*, No. 44, 51, 1938.

# A Study of the Reactions between Dolomite and Various Minerals (Cont.).

## Part II.—X-Ray Examination of the Dolomite B-Steatite A Series.*

By J. R. RAIT, B.Sc., PH.D., A.R.T.C., and
H. J. GOLDSCHMIDT, M.Sc.

ABSTRACT.

Fired dolomite–steatite mixtures containing initially from 0 to 15 per cent. of steatite and two commercial dolomite bricks have been submitted to X-ray analysis using a Debye-Scherrer camera. The relative intensities of characteristic lines have been measured photometrically. Qualitatively and quantitatively, within the limits of accuracy of the method, the results for the mineralogical constitution of the sinters are in complete accord with those deduced in Part I on the basis of determinations of free lime and consideration of the appropriate thermal equilibrium diagrams.

For the particular dolomite and steatite investigated the proportion of free lime present in the fired mixes decreased to nil as the initial steatite content increased to between 8 and 10 per cent., at which composition there was the maximum production of $3CaO.SiO_2$. Further addition of steatite resulted in a decrease in the amount of this constituent and a corresponding increase in the proportion of $2CaO.SiO_2$. The magnesia was present in almost constant amount as uncombined periclase.

In a previous study,[1] a series of mixtures of dolomite B–steatite A was fired in a gas-fired furnace to about 1,500° C. The resulting products were analysed qualitatively and quantitatively for uncombined lime and the steam hydration indices were determined. The percentage analyses of the materials were as follows :

|  | CaO. | MgO. | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | $TiO_2$. | Loss on ignition. |
|---|---|---|---|---|---|---|---|
| Dolomite B | 29·27 | 20·02 | 3·86 | 0·99 | 0·98 | 0·12 | 44·45 |
| Steatite A | 0·34 | 31·59 | 60·76 | 1·08 | 1·01 | — | 4·40 |

The analyses of the calcined mixtures are given in Table XII.

It was found possible to calculate the constitution of these mixtures by means of the available thermal equilibrium data.[1] The results of these calculations are given in Table XIII.

The calculated and experimental free lime results agreed closely and a satisfactory explanation of the steam hydration

TABLE XII.—PERCENTAGE COMPOSITION OF FIRED MIXTURES.

| Mix. | Uncalcined. | | CaO. | SiO$_2$. | MgO. | Al$_2$O$_3$. | Fe$_2$O$_3$. |
|---|---|---|---|---|---|---|---|
| | Dolomite B, per cent. | Steatite A, per cent. | | | | | |
| 1 | 100 | ·0 | 52·60 | 6·94 | 36·0 | 1·78 | 1·76 |
| 2 | 98 | 2 | 50·90 | 8·86 | 35·9 | 1·76 | 1·74 |
| 3 | 96 | 4 | 49·17 | 10·74 | 35·8 | 1·74 | 1·72 |
| 4 | 94 | 6 | 47·40 | 12·52 | 35·67 | 1·72 | 1·69 |
| 5 | 92 | 8 | 45·83 | 14·32 | 35·62 | 1·70 | 1·67 |
| 6 | 90 | 10 | 44·17 | 16·01 | 35·47 | 1·68 | 1·65 |
| 7 | 88 | 12 | 42·68 | 17·71 | 35·44 | 1·66 | 1·63 |
| 8 | 85 | 15 | 40·41 | 20·14 | 35·32 | 1·63 | 1·60 |
| Dolomite Brick | .. | .. | 37·80 | 15·92 | 40·68 | 1·02 | 3·62 |

TABLE XIII.—CALCULATED MINERALOGICAL CONSTITUTION OF FIRED MIXTURES (WEIGHT PER CENT.).

| Mix. | Free CaO. | MgO. | 3CaO. SiO$_2$. | 2CaO. SiO$_2$. | 4CaO.Al$_2$O$_3$. Fe$_2$O$_3$. | 3CaO. Al$_2$O$_3$. | 5CaO. 3Al$_2$O$_3$. | 2CaO. Fe$_2$O$_3$. |
|---|---|---|---|---|---|---|---|---|
| 1 | 29·64 | 36·0 | 26·42 | — | 5·35 | 1·72 | — | — |
| 2 | 22·59 | 35·9 | 33·66 | — | 5·29 | 1·72 | — | — |
| 3 | 15·64 | 35·8 | 40·81 | — | 5·23 | 1·69 | — | — |
| 4 | 8·99 | 35·67 | 47·52 | — | 5·13 | 1·69 | — | — |
| 5 | ·4·04 | 35·62 | 52·72 | — | 5·07 | 1·69 | — | — |
| 6 | — | 35·47 | 44·61 | 12·21 | 5·01 | 1·66 | — | — |
| 7 | — | 35·44 | 25·69 | 31·39 | 4·94 | 1·66 | — | — |
| 8 | — | 35·32 | — | 57·74 | 4·86 | 0·08 | 1·11 | — |
| Dolomite brick | — | 40·7 | 18·0 | 32·1 | 4·9 | — | — | 3·4 |

curves was obtained.    However, as discussed in Part I, the five component thermal equilibrium diagram CaO–MgO–SiO$_2$–Al$_2$O$_3$–Fe$_2$O$_3$ should be known to make possible the calculation of the constitution of these dolomite-steatite mixtures and the dolomite brick.    Unfortunately, this diagram has not yet been investigated, but from a study of the available data it was considered very probable that in all the mixtures examined all the magnesia would crystallise as the primary phase in the form of periclase.    On this assumption it was then possible to calculate the constitutions from the quaternary diagram CaO–2CaO.SiO$_2$–5CaO.3Al$_2$O$_3$–4CaO.Al$_2$O$_3$. Fe$_2$O$_3$ which had been very systematically determined by F. M. Lea and T. W. Parker.[2]    Although the constitutions of a large number

of mixtures of dolomite with various magnesium silicate and siliceous minerals calculated on this assumption gave free lime results similar to those found experimentally and provided a satisfactory explanation of the steam hydration curves, it was considered that further justification of this assumption would be very desirable. The X-ray diffraction method appeared to offer the best means of identifying phases and at the same time indicating their relative amounts.

It is only comparatively recently that X-ray methods have been applied to the study of ceramic materials; although a considerable number of investigations have already been made, most of them are qualitative or semi-quantitative. L. Navias [3] studied mullite in fired bodies, and A. J. Bradley and A. L. Roussin [4] surveyed porcelains in their relation to mullite. L. T. Brownmiller and R. H. Bogue [5] applied the X-ray method to the constitution of Portland cements, while recently J. Ch. L. Favejee [6] analysed soils by X-rays, emphasising the quantitative factors and incidentally giving a valuable bibliography on the subject. Notable contributions to our knowledge of refractories have been made by A. H. Jay [7] and B. J. Pines and K. I. Dorogoj [8]. Recently, J. White and J. Grieve [9] have successfully applied X-ray methods to the slag system $FeO-TiO_2$.

EXPERIMENTAL PROCEDURE.

The powder method with a 9-cm. diameter Debye-Scherrer camera and Co $K\alpha$ radiation was employed. It is not proposed to describe this method, since full information regarding it may be found elsewhere.[10] All the samples which tend to hydrate were calcined previous to the X-ray exposures and precautions were taken to prevent subsequent contact with moisture. The usual procedure of mixing the powder to a fine paste with Canada balsam and mounting on a fine hair suspended in the centre of the camera, was found to be quite satisfactory. A series of standard photographs of pure calcined CaO, periclase (magnesite brick), $3CaO.SiO_2$, $\beta$-$2CaO.SiO_2$, $\gamma$-$2CaO.SiO_2$, and $4CaO.Al_2O_3.Fe_2O_3$ was taken. Photographs of the various members of the series and of the dolomite brick were prepared in a similar fashion. By comparing each of these latter photographs with the standards it was found possible to account for all the lines and to identify the various crystalline constituents in each case.

PREPARATION OF THE STANDARDS.

$3CaO.SiO_2$.—Pure $CaCO_3$ and $SiO_2$ were thoroughly mixed in the correct proportions, bonded with collodion, and fired in a gas-fired furnace. This material was crushed and refired until a homogeneous material was obtained.

$\gamma$-$2CaO.SiO_2$.—This was prepared in a similar fashion. On

cooling through 675° C. the material " dusted " to a fine white powder.

$\beta$-2CaO.SiO$_2$.—Pure CaCO$_3$ and SiO$_2$ were mixed in the correct proportions with about 0·5 per cent. B$_2$O$_3$ and fired as for the other materials.    No " dusting " occurred on cooling through 675° C.

$4CaO.Al_2O_3.Fe_2O_3$.—Pure CaCO$_3$, Al$_2$O$_3$, and Fe$_2$O$_3$ were thoroughly mixed, bonded with collodion, and fired to within a few degrees of the melting-point.

$CaO$.—Pure CaO was prepared by calcining CaCO$_3$.

$MgO$.—Since a magnesite brick consists chiefly of periclase, this was used as a standard.    Comparison with the pure magnesia pattern showed that there were in addition a few faint lines which were probably due to magnesium silicates or ferrite.

Pure samples of 3CaO.SiO$_2$, $\beta$-2CaO.SiO$_2$, $\gamma$-2CaO.SiO$_2$, and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ were kindly supplied by the Building Research Station.[2]    The X-ray patterns of their materials corresponded to those prepared as above.

Periclase (MgO) has the cubic structure of the rock salt type. The side of the cube is 4·20Å.

CaO has the same structure, but the lattice spacing is 4·80Å.

The patterns of the silicates and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, in contrast to those of CaO and MgO, are much more complicated, consisting of a large number of lines, but each pattern is quite characteristic, although the silicates show certain similarities in their patterns. The X-ray photographs of the materials and the dolomite brick are reproduced in Fig. 10 (Plate II).

QUANTITATIVE ESTIMATION OF CONSTITUENTS.

The relative intensities of reflections due to the different crystalline constituents in the mixture can serve as a measure of their relative amounts, but in attempting to apply this principle it is necessary to discuss briefly certain difficulties inherent in the method which limit its scope.

1. Since the X-ray can only detect crystalline phases, any compounds in the amorphous (glassy) state will evade observation, except when present in considerable amounts so as to produce a distinct halo.    Some glassy material is liable to occur in the substances under examination, and therefore although all observed lines can be accounted for by one or other of the crystalline phases, the sum of these phases does not necessarily correspond to the total number in the material.    However, the glassy material is apt to indicate its presence by adding to the background of the photograph.

2. The lower limit of visibility of each phase depends on its crystalline nature as well as factors of photographic technique. L. T. Brownmiller and R. H. Bogue [5] in their investigation of

cooling through 675° C. the material " dusted " to a fine white powder.

$\beta$-2CaO.SiO$_2$.—Pure CaCO$_3$ and SiO$_2$ were mixed in the correct proportions with about 0·5 per cent. B$_2$O$_3$ and fired as for the other materials. No " dusting " occurred on cooling through 675° C.

$4CaO.Al_2O_3.Fe_2O_3$.—Pure CaCO$_3$, Al$_2$O$_3$, and Fe$_2$O$_3$ were thoroughly mixed, bonded with collodion, and fired to within a few degrees of the melting-point.

$CaO$.—Pure CaO was prepared by calcining CaCO$_3$.

$MgO$.—Since a magnesite brick consists chiefly of periclase, this was used as a standard. Comparison with the pure magnesia pattern showed that there were in addition a few faint lines which were probably due to magnesium silicates or ferrite.

Pure samples of 3CaO.SiO$_2$, $\beta$-2CaO.SiO$_2$, $\gamma$-2CaO.SiO$_2$, and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ were kindly supplied by the Building Research Station.[2] The X-ray patterns of their materials corresponded to those prepared as above.

Periclase (MgO) has the cubic structure of the rock salt type. The side of the cube is 4·20Å.

CaO has the same structure, but the lattice spacing is 4·80Å.

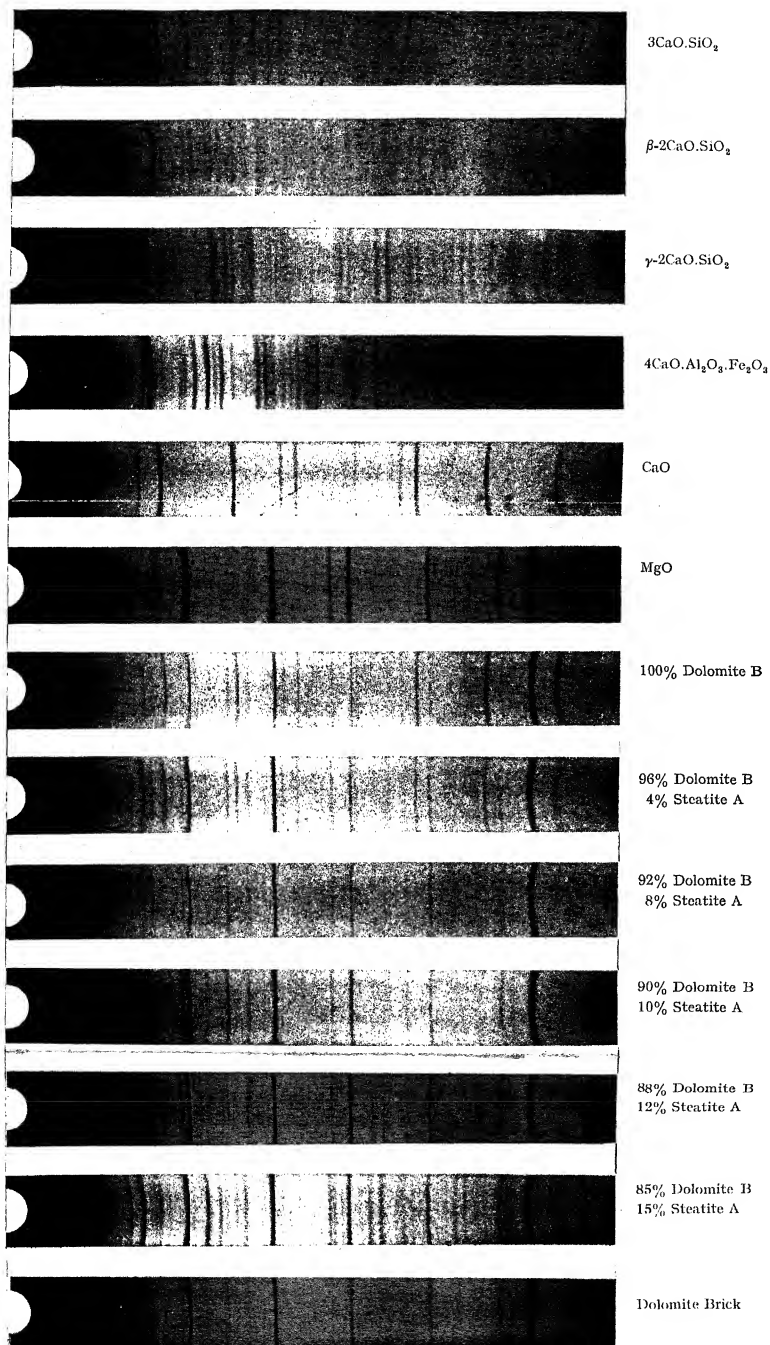The patterns of the silicates and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, in contrast to those of CaO and MgO, are much more complicated, consisting of a large number of lines, but each pattern is quite characteristic, although the silicates show certain similarities in their patterns. The X-ray photographs of the materials and the dolomite brick are reproduced in Fig. 10 (Plate II).

### QUANTITATIVE ESTIMATION OF CONSTITUENTS.

The relative intensities of reflections due to the different crystalline constituents in the mixture can serve as a measure of their relative amounts, but in attempting to apply this principle it is necessary to discuss briefly certain difficulties inherent in the method which limit its scope.

1. Since the X-ray can only detect crystalline phases, any compounds in the amorphous (glassy) state will evade observation, except when present in considerable amounts so as to produce a distinct halo. Some glassy material is liable to occur in the substances under examination, and therefore although all observed lines can be accounted for by one or other of the crystalline phases, the sum of these phases does not necessarily correspond to the total number in the material. However, the glassy material is apt to indicate its presence by adding to the background of the photograph.

2. The lower limit of visibility of each phase depends on its crystalline nature as well as factors of photographic technique. L. T. Brownmiller and R. H. Bogue [5] in their investigation of

B

3CaO.SiO₂

β-2CaO.SiO₂

γ-2CaO.SiO₂

4CaO.Al₂O₃.Fe₂O₃

CaO

MgO

100% Dolomite B

96% Dolomite B
4% Steatite A

92% Dolomite B
8% Steatite A

90% Dolomite B
10% Steatite A

88% Dolomite B
12% Steatite A

85% Dolomite B
15% Steatite A

Dolomite Brick

PLATE II.

10.—Debye-Scherrer X-ray photographs indicating compounds present in fired dolomite mixes.

cements stated the lower limits of visibility of the constituent phases found therein as follows :

| | |
|---|---|
| CaO .. .. .. .. .. .. | 2·5 per cent. |
| MgO .. .. .. .. .. .. | 2·5 ,, |
| $3CaO.Al_2O_3$ .. .. .. .. .. | 6 ,, |
| $3CaO.SiO_2$ .. .. .. .. .. | 8 ,, |
| $4CaO.Al_2O_3.Fe_2O_3$ .. .. .. .. | 15 ,, |
| $2CaO.SiO_2$ .. .. .. .. .. | 15 ,, |

Although these figures cannot be taken in any way as exact and must be considered with reserve, they may form a guide for the order of magnitude in the present work. For CaO and MgO the lower limit of visibility can be taken in our case as between 2 and 5 per cent., but somewhat higher for the remaining phases. The only satisfactory way of determining it is by examination of a series of synthetic mixtures. It is intended to develop this more quantitative side in future work, but at present it will suffice to indicate the order of magnitude of the lower visibility limit.

If the crystallite size of any constituent phase is below $10^{-5}$ cm., line broadening becomes appreciable, the higher angle reflections may disappear entirely, suggesting absence of the phase contrary to the fact. In our case it does not seem to enter seriously, as can be seen by the patterns, which are sharp and distinct up to high angles.

3. The crystal structures of the silicates in question are of very low symmetry, the patterns thus produced being very rich in lines, many of which coincide either wholly or partly. For correct quantitative interpretation care must be taken to identify and utilise only lines, not always easy to find, which can be uniquely attributed to the phase. However, after closer scrutiny even coincident lines can be taken as a useful additional measure·; examples arise in the present work. A low order reflection of lime and one due to $3CaO.SiO_2$ coincide. Following this line through the series from 100 to 90 per cent. dolomite, its intensity remains approximately constant. Different order reflections due to these two phases reveal a steady decrease of lime and a steady increase of $3CaO.SiO_2$.

4. Although the integrated intensity of a line naturally increases with increasing percentage of the constituent producing it, this increase cannot strictly be taken as a proportional one. This fact has been demonstrated by J. Ch. L. Favejee,[6] who experimented with soil mixtures of known constitution, showing that the assumption of proportionality is not generally justified. The law giving intensity as a function of amount of the phase differs with the crystal plane producing the line, for some lines the increase being more, for others less than proportional. Lines of moderate intensity are the most suitable for quantitative estimates. The direct method of determining the amount of a phase $x$ in a mixture

by comparing its intensities with those of a photograph of pure $x$ is subject to considerable inherent errors, even if the photographic conditions were identical.   Strictly, it is necessary for each case of two or more co-existing phases to find the relation between amount of material and line intensity by means of synthetic mixtures. However, although these limitations must be considered, their effect can largely be eliminated by check and cross-check using different lines.   Our aim is essentially to state :

(a) Whether a phase is present or not.

(b) Whether it increases, decreases, or remains constant.

(c) To obtain an approximate idea as to quantities.

5. In considering quantitative measurement of the intensities of lines produced by the crystalline powder, absorption and atomic scattering power enter prominently.   This has an effect on the intensity of the diffraction lines as well as on the background blackness.   Details can be found in the work of J. C. M. Brentano [11] and A. J. Bradley,[12] among others.   Although absorption can only be minimised by making the diameter of the powder specimen very small, its concentration low, and particle size as fine as possible (about $10^{-4}$ to $10^{-3}$ cm.), we are mainly concerned with reducing the difference in absorption between the members of the series. The specimen diameter was 0·5 mm. and attention was paid to particle size and uniformity of concentration.   Further, to ensure comparability of the photographs the milliamp-minutes during exposure had, of course, to be the same.

Although the study of the photographs (Fig. 10) plainly revealed the change of phases as set out in Table XV, it was considered advisable to take photometer records showing more clearly the tendencies thus disclosed.   A simple microphotometer was constructed for this purpose.   Light of standardised intensity through a narrow slit was focused on to the film and received by a Weston barrier layer type of photoelectric cell (Photronic cell).   The galvanometer deflection served as a direct measure of blackness.   Film displacements were recorded accurately to 0·0025 mm.   The actual interval of readings was 1/10 mm.   Fig. 11 shows the photometer records. The same low angle range on all films was chosen, approx. 2 cm. in length, which contains characteristic lines of each phase.   The range extended from A to B (Fig. 10).   Records are given of the pure phases for reference along with the dolomite–steatite series and the two dolomite bricks.   All photometer curves are arranged so that corresponding points are vertically aligned.

EXPERIMENTAL RESULTS.

Qualitative examination of the photographs and photometer records gave the following constitutions :

100 *per cent. Dolomite B.*
     Periclase, lime, and $3CaO.SiO$ .

*96 per cent. Dolomite B–4 per cent. Steatite A.*
   Periclase, lime, and $3CaO.SiO_2$.
*90 per cent. Dolomite B–10 per cent. Steatite A.*
   Periclase, $3CaO.SiO_2$, and $\beta$-$2CaO.SiO_2$.
*88 per cent. Dolomite B–12 per cent. Steatite A.*
   Periclase, $3CaO.SiO_2$, and $\beta$-$2CaO.SiO_2$.
*85 per cent. Dolomite B–15 per cent. Steatite A.*
   Periclase, $3CaO.SiO_2$, and $\gamma$-$2CaO.SiO_2$.
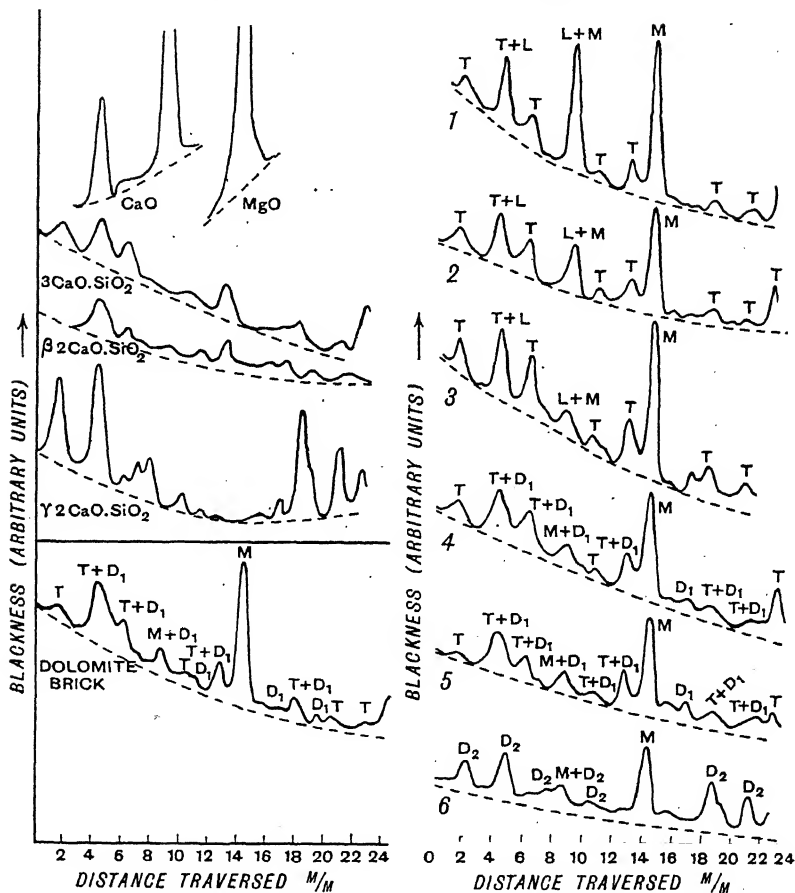


Fig. 11.—Photometer curve of region A to B in Fig. 10.
(1) 100 per cent. dolomite B.
(2)  96    ,,       ,,    B– 4 per cent. steatite A.
(3)  92    ,,       ,,    B– 8   ,,    ,,    A.
(4)  90    ,,       ,,    B–10   ,,    ,,    A.
(5)  88    ,,       ,,    B–12   ,,    ,,    A.
(6)  85    ,,       ,,    B–15   ,,    ,,    A.
T—$3CaO.SiO_2$.  L—CaO.  M—MgO.  $D_1$—$\beta 2CaO.SiO_2$.  $D_2$—$\gamma 2CaO.SiO_2$.

PHOTOMETER CURVES.

With the information derived from the photographs and the photometer curves of the standards, each of the peaks in the photometer curves of the dolomite-steatite series and of the dolomite brick (see Fig. 11) has been named according to the phase which they represent. It will be seen that many reflections due to different constituents coincide, in particular those of $3CaO.SiO_2$, $\beta$-$2CaO.SiO_2$, and $\gamma$-$2CaO.SiO_2$, which are very rich in lines. Nevertheless, characteristic lines of each phase are present and can be used for comparison, and even coincident lines can be employed for comparative purposes. The strong reflection (220) of periclase is the most prominent throughout the series, while lime is represented by two reflections (111) and (220); although the former coincides with a line of $3CaO.SiO_2$ and the latter with a line of periclase, they reveal the decreasing content of lime from 100 to 92 per cent. dolomite. It must be remembered that not the heights of the peaks but the areas represent the line intensity. The approximate background intensity has been inserted to facilitate the estimation. It is possible to represent the relative amounts of phases present in each member of the series by measuring the areas under characteristic lines. These figures are in arbitrary units. They are subject to the experimental errors previously outlined, in particular the intense periclase line. The results are shown in Table XIV.

TABLE XIV.—RELATIVE INTENSITIES OF CHARACTERISTIC LINES OF COMPOUNDS PRESENT.

| Line. | Fired Dolomite B–Steatite A Mixes. | | | | | | Dolomite Brick |
| --- | --- | --- | --- | --- | --- | --- | --- |
| | 1 | 3 | 5 | 6 | 7 | 8 | |
| MgO (220) | 150 | 135 | 175 | 140 | 130 | (95) | 170 |
| MgO (311) | 35 | 30 | 45 | 35 | 30 | (35) | 45 |
| $3CaO.SiO_2$ | 20 | 40 | 50 | 35 | 15 | — | 25 |
| $CaO+MgO$ | 140 | 70 | 33 | — | — | — | • |
| $\beta$-$2CaO.SiO_2$ +MgO. | — | — | — | 30 | 35 | — | 30 |

The experimental results are summarised in Table XV.

Comparison of Tables XIII and XV reveals that the X-ray ₁dings are in harmony with the calculated results based on phase equilibria.

(a) Subject to the experimental error of the method, the periclase content remains constant throughout the series. It has been estimated from the relative intensities that the periclase content is between 30 and 50 per cent. By calculation it has been shown to be between 35 and 36 per cent. Further evidence that all the

MgO exists as periclase is obtained with the variation of other phases which is exactly similar to that forecast by the calculations.

(b) The free lime decreases from mixes 1 to 5, mix 5 only showing a trace (2–5 per cent.). Similar results were obtained by calculation, mix 5 having a free lime content of 4 per cent. Quantitative free lime analysis further verified this result. Proceeding through the series from mix 5, no free lime was detected by X-rays. Since the lower limit of visibility is 2 to 5 per cent., the X-ray evidence therefore proves that less than 2 to 5 per cent. free lime occurs. However, quantitative free lime analysis and calculation show that free lime does not exist beyond mix 5.

(c) Proceeding through the series, the $3CaO.SiO_2$ content increases to a maximum, as free lime decreases to zero. As the $2CaO.SiO_2$ content increases to a maximum the $3CaO.SiO_2$ decreases, no trace of $3CaO.SiO_2$ being found in mix 8. Again the lower limit of visibility must be considered. In mix 8 there is less than the visibility limit of $3CaO.SiO_2$. It does not follow directly that there is no $3CaO.SiO_2$. Similarly, in mixes 1 to 5 there is less than the visibility limit of $2CaO.SiO_2$. However, the variation of these phases through the series as found by X-rays is exactly similar to that found by calculation on the phase equilibria and the quantitative free lime analysis. Mix 8, which contains $\gamma$-$2CaO.SiO_2$, "dusted" completely. No trace of dusting was found in the other materials, which further verifies the X-ray results.

(d) The $\beta$ and $\gamma$ modifications of $2CaO.SiO_2$ were readily distinguished by the X-ray method. The $\beta$ type is present in mixes 6 and 7 and the $\gamma$ form in mix 8. On cooling through 675° C. the $\beta$ to $\gamma$ transformation occurs with a 10 per cent. expansion which causes a material with a high content of $2CaO.SiO_2$ to fall to dust. It was not possible to differentiate between the $\beta$ and $\gamma$ forms by calculation.

(e) The X-ray photographs and photometer records show that there is an approximate comparison between the dolomite brick and the clinker 88 per cent. dolomite B–12 per cent. steatite A. Examination of Table XIII reveals that their calculated mineral contents are also somewhat similar.

(f) The percentage contents of all the other compounds shown to be present by calculation, namely, $4CaO.Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $2CaO.Fe_2O_3$ are definitely below the visibility limit of the X-ray powder method.

No one method of approach to the complicated problem of the constitution of stabilised dolomite clinkers may be regarded, of itself, as altogether conclusive. The separation of the compounds from a finely ground sample based on differences in specific gravity presents considerable difficulties. L. T. Brownmiller and R. H. Bogue [5] found that the intimate intergrowth of the crystal phases in cement militated against such a mode of investigation. Microscopic examinations are probably satisfactory on specially prepared

TABLE XV.—SUMMARY OF RESULTS OF X-RAY ANALYSIS.

| Mix. | Dolomite B, per cent. | Steatite A, per cent. | Free CaO. | Periclase. | $3CaO.SiO_2$. | $2CaO.SiO_2$. |
|---|---|---|---|---|---|---|
| 1 | 100 | 0 | Present (medium) | Present.* | Present. | Absent. |
| 3 | 96 | 4 | Present (small to medium). | Present.* | Present. | Absent. |
| 5 | 92 | 8 | Present (trace). | Present.* | Present. ↓ Max. | Absent. |
| 6 | 90 | 10 | Absent. | Present.* | Present. ↑ | Present ($\beta$). |
| 7 | 88 | 12 | Absent. | Present.* | Present. | Present ($\beta$). |
| 8 | 85 | 15 | Absent. | Present.* | Absent. | Present Max. ($\gamma$). |
| Dolomite brick | .. | .. | Absent. | Present. | Present. | Present ($\beta$). |

* Approximately constant (30–50 per cent.).

laboratory clinkers, but the fineness of the structure of commercial dolomite clinkers makes such a study rather difficult. Calculations based on the phase-rule interpretations of chemical analysis may be criticised on the grounds that the exact state of the equilibrium which obtains is not known ; further, the five-component system $CaO–SiO_2–Al_2O_3–MgO–Fe_2O_3$ has not yet been thoroughly investigated. However, calculations based on the phase equilibria gave results exactly similar to those obtained by quantitative free lime analysis and explained the form of the steam hydration curves.[1] The X-ray method by itself is also inconclusive because of its limitation in detecting small amounts of phases and glassy material.

However, all the data obtained by steam hydration investigations, quantitative free lime analysis, phase equilibria, and X-ray methods are in perfect agreement, no case existing where the results of different methods are in conflict.

CONSTITUTION OF COMMERCIAL DOLOMITE REFRACTORIES.

The constitution of a dolomite brick cannot be completely determined by the X-ray powder method without the calculations based on phase equilibria. The X-ray results indicate what are the chief constituents. However, it is necessary to resort to phase equilibria calculations to find the amounts of these phases ; further, it is only by the latter methods that the presence and the amounts of $4CaO.Al_2O_3.Fe_2O_3$ and $3CaO.Al_2O_3$ can be determined. The X-ray method shows that periclase, $3CaO.SiO_2$, and $2CaO.SiO_2$ are the chief constituents of the dolomite brick examined, but the

small amounts of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$ are only revealed by calculation.

The important conclusion may be drawn from the investigations of Part I and II that the constitution of dolomite, stabilised by steatites, serpentines, or the various forms of silica as described in Part I, can be calculated from their chemical analysis on the basis of phase equilibria.

The dolomite brick has now assumed great importance in the steel industry due to the present shortage of magnesite. The brick examined can be stored indefinitely without serious danger of hydration and has been successfully used in steel-furnace hearths. Attempts are now being made to improve their performance in exposed parts of the furnace. It is considered by the authors that the clue to the problem is probably closely connected with the constitution and the mechanism of the reaction between the raw dolomite and the stabiliser. A systematic study of each of the constituent phases would undoubtedly augment our knowledge of the modern dolomite refractory. For example, the compound $4CaO.Al_2O_3.Fe_2O_3$ has a melting-point of about $1,420°$ C.; further, there is an invariant point in the $CaO–2CaO.SiO_2–5CaO.3Al_2O_3–4CaO.Al_2O_3.Fe_2O_3$ diagram at $1,338°$ C. at a composition 54·8 per cent. CaO, 22·7 per cent. $Al_2O_3$, 6 per cent. $SiO_2$, 16·5 per cent. $Fe_2O_3$. Without going into full details, it can be stated that low contents of $Al_2O_3$ and $Fe_2O_3$ in the dolomite and stabiliser are necessary for high refractoriness. $3CaO.SiO_2$, which is fairly abundant in the dolomite brick tested has been proved to be unstable. Above $1,900°$ and below $1,300°$ C. it dissociates as follows :

$$3CaO.SiO_2 \rightarrow 2CaO.SiO_2 + CaO$$

E. T. Carlson [13] heated $3CaO.SiO_2$ for a standard time at different temperatures, the resulting product being analysed for free lime. A graph was obtained of free lime against temperature which showed amounts of free lime rising to a maximum at $1,175°$ C. and falling away, with increasing temperature becoming practically zero at $1,300°$ C. F. M. Lea and T. W. Parker [2] investigated the decomposition of pure $3CaO.SiO_2$ and $3CaO.SiO_2$ in quaternary melts. Their results are shown in Table XVI.

F. M. Lea and T. W. Parker [2] concluded that the lower decomposition temperature of $3CaO.SiO_2$ occurs at $1,250 \pm 25°$ C. The rate of decomposition is fairly slow. In the steel furnace part of the brick will be held at $1,250°$ C. over long periods ; decomposition of the $3CaO.SiO_2$ might lead to cracking and failure. Here is a field for further research.

$2CaO.SiO_2$ on cooling transforms from the $\beta \rightarrow \gamma$ modification at $675°$ C.; a 10 per cent. expansion accompanies this transformation, causing the material to fall to a fine powder. Small additions of various materials suppress this transformation. For example, 0·5 per cent. $B_2O_3$ is sufficient to maintain the $2CaO.SiO_2$ in the $\beta$ form

5

down to room temperature. The authors have verified this by X-ray photographs. Small additions of $B_2O_3$ to the dolomite clinker sometimes produce a green stain on the surface. Such stains have frequently been found on the surface of dolomite bricks ; the X-ray photograph has shown the $2CaO.SiO_2$ to be in the $\beta$ form. It is therefore very probable that small amounts of $B_2O_3$ are added in the clinkering process. There appears to be no information in the literature concerning the permanency of the effect of $B_2O_3$ in maintaining $2CaO.SiO_2$ in the $\beta$ form. This offers a further interesting field for research.

TABLE XVI.—RESULTS OF F. M. LEA AND T. W. PARKER ON THE THERMAL DECOMPOSITION OF $3CaO.SiO_2$ ALONE AND IN QUATERNARY MELTS.

| Composition. | | | | Temp. of Heating, °C. | Time of Heating (hours). | Free lime Developed (per cent.). | $3CaO.SiO_2$ Decomposed (per cent.). |
|---|---|---|---|---|---|---|---|
| CaO. | $Al_2O_3$. | $SiO_2$. | $Fe_2O_3$. | | | | |
| 60·2 | 17·8 | 12·0 | 10 | 1,150 | 240 | 3·84 | 76·9 |
| | | | | 1,175 | 48 | 0·54 | 10·8 |
| | | | | | 240 | 3·84 | 76·9 |
| | | | | 1,175 | 150 | 3·54 | 70·9 |
| | | | | | 300 | 4·62 | 92·5 |
| | | | | 1,225 | 220 | 1·2 | 24·0 |
| | | | | 1,250 | 48 | 0 | 0 |
| | | | | 1,300 | 90 | 0 | 0 |
| 60·6 | 17·4 | 12·0 | 10 | 1,225 | 100 | 0·3 | 5·0 |
| | | | | | 200 | 3·1 | 51·6 |
| | | | | | 300 | 4·0 | 66·7 |
| | | | | 1,250 | 100 | 1·0 | 16·7 |
| | | | | | 200 | 0 | 0 |
| | | | | | 300 | 1·0 | 16·7 |
| | | | | 1,300 | 100 | 0 | 0 |
| | | | | 1,350 | 100 | 0 | 0 |
| $3CaO.SiO_2$ | | | | 1,175 | 108 | 1·9 | 7·7 |
| | | | | | 300 | 4·4 | 17·9 |
| | | | | | 640 | 21·0 | 85·5 |
| | | | | 1,200 | 200 | 15·5 | 63·0 |
| | | | | 1,225 | 100 | 1·0 | 4·0 |
| | | | | | 150 | 4·0 | 17·1 |
| | | | | 1,250 | 120 | 0 | 0 |
| | | | | 1,275 | 140 | 0 | 0 |

The X-ray examination of the other dolomite series [1] is now being undertaken.

REFERENCES.

1. J. R. Rait and A. T. Green, this Report, p. 13.
2. F. M. Lea and T. W. Parker, *Phil. Trans. Roy. Soc.*, 234, 1, 1934.
3. L. Navias, *J. Amer. Ceram. Soc.*, 8, 296, 1925.

4. A. J. Bradley and A. L. Roussin, *Trans. Ceram. Soc.*, **31,** 422, 1932.
5. L. T. Brownmiller and R. H. Bogue, *Amer. J. Sci.*, **20,** 241, 1930.
6. J. Ch. L. Favejee, *Zeit. Krist.*, **101,** 259, 1939.
7. A. H. Jay, *Trans. Ceram. Soc.*, **38,** 455, 1939 ; A. H. Jay and J. H Chesters, *ibid.*, **37,** 209, 1938.
8. B. J. Pines and K. I. Dorogoj, *Ogneupory*, **3,** 603, 1937.
9. J. White and J. Grieve, *J. Roy. Tech. Coll. Glasgow*, **4,** 441, 1939.
10. W. H. Bragg and W. L. Bragg, " The Crystalline State," Vol. 1 ; G. L Clark, " Applied X-rays."
11. J. C. M. Brentano, *Proc. Phys. Soc.*, **47,** 932, 1935 ; **50,** 247, 1938.
12. A. J. Bradley, *ibid.*, **47,** 879, 1935.
13. E. T. Carlson, *Bureau Standards J. Research*, **7,** 893, 1931.

# A Study of the Reactions between Dolomite and Various Minerals (Cont.).

## Part III.—Further X-Ray Examinations.*

By J. R. RAIT, B.Sc., Ph.D., A.R.T.C., and
H. J. GOLDSCHMIDT, M.Sc.

ABSTRACT.

In Part I, the mineralogical constitutions of a number of clinkers, pre-pared by calcining mixtures of dolomite and various proportions of four different steatites, flint, serpentine, olivine, bentonite, china clay, alumina and ferric oxide were deduced from a consideration of the free lime contents, hydration curves and of the appropriate thermal equilibrium diagrams. The clinkers have now been submitted to X-ray analysis using a Debye-Scherrer camera. The results are in complete accord with the constitutions previously assigned, and confirm the assumptions made regarding certain of the relevant four- and five-component systems. The evidence indicates a close approach to chemical equilibrium in the experimental clinkers and in commercial dolomite products. The results of the X-ray analysis and the calculated mineralogical composition of three commercial products are likewise in close agreement.

INTRODUCTION.

In a previous investigation,[1] mixtures in various proportions of dolomite and flint, steatites, olivine, serpentine, bentonite, china clay, alumina, ferric oxide, open-hearth slag, zircon, zirconia, baddeleyite, rutile, chromium oxide and chromites were fired to high temperatures. The fired clinkers were qualitatively tested for the presence of free lime and quantitative determinations made on numerous samples. The hydration indices of the clinkers were also measured.

From consideration of the relevant thermal equilibrium dia-grams, assuming that the reactions in the clinkers had proceeded to equilibrium, the mineral constitutions of the clinkers were cal-culated. The results of these calculations were substantiated by (a) comparison of the calculated and experimentally determined free lime contents; (b) the " dusting " of those clinkers which calculation indicated had a high content of $2CaO.SiO_2$; (c) tl

* *Bull. B.R R.A.*, **58**, 95, 1941.

63

form of the curves obtained by plotting the steam hydration indices against the percentage acidic oxides.

Although the results of the calculations were confirmed as described above, it was considered that further evidence should be obtained, since complete thermal equilibrium data were not available. The X-ray powder method offered the possibility of identifying the phases and at the same time indicating their relative amounts. In this study, the various series of mixes have been classified into the following groups :—

(1) Dolomite B with various proportions of four different steatites, and with serpentine, flint, olivine, bentonite, china clay, alumina and ferric oxide. Mixes of dolomite A with various proportions of steatite A were included in this group.

(2) Dolomite B with acid open-hearth slag.

(3) Dolomite B with various zirconium and titanium compounds.

(4) Dolomite B with chromium oxide and various chromites.

In a preliminary investigation [2] the dolomite B—steatite A series was examined by means of the X-ray powder method. The technique, which was described, has been used in the present investigations dealing with the remaining series of group 1.

MATERIALS OF INVESTIGATION.

The analyses of the materials are given in Table XVII.

TABLE XVII.—PERCENTAGE ANALYSES OF MATERIALS USED.

|  | $CaO.$ | $MgO.$ | $SiO_2.$ | $Al_2O_3.$ | $Fe_2O_3.$ | $Cr_2O_3.$ | $TiO_2.$ | Loss on Ignition. |
|---|---|---|---|---|---|---|---|---|
| Dolomite A.. | 50·50 | 34·94 | 3·22 | 1·04 | 3·06 | — | 0·20 | 6·64 |
| Dolomite B.. | 29·27 | 20·00 | 3·86 | 0·99 | 0·98 | — | 0·12 | 44·45 |
| Flint .. | — | — | 98·30 | — | — | — | . — | — |
| Steatite A.T.1 | 0·60 | 32·70 | 36·90 | 1·34 | 6·40 | — | — | 21·60 |
| Steatite F.G.X.O... | 3·28 | 29·19 | 38·37 | 4·95 | 7·26 | — | 0·48 | 16·33 |
| Steatite 3B.. | 0·81 | 30·00 | 46·18 | 10·72 | 2·06 | — | 0·55 | 8·35 |
| Olivine .. | 0·26 | 48·98 | 40·34 | 2·22 | 6·09 | — | 0·12 | 2·01 |
| Serpentine .. | 0·33 | 35·30 | 31·01 | 3·72 | 10·06 | 6·22 | 0·18 | 13·24 |
| Bentonite .. | 0·87 | 2·12 | 52·66 | 18·42 | 3·19 | — | 0·19 | 19·52 |
| China Clay .. | 0·13 | 0·31 | 46·86 | 38·42 | 0·44 | — | — | 12·42 |
| Alumina .. | — | — | — | 100 | — | — | — | — |
| Ferric Oxide | — | — | — | — | 100 | — | — | — |

PREPARATION OF THE STANDARDS.

The preparation of $3CaO.SiO_2$, $\beta$- and $\gamma$-$2CaO.SiO_2$, $4CaO.Al_2O_3$. $Fe_2O_3$, CaO and periclase has been described elsewhere.[2]

The binary system CaO–Fe$_2$O$_3$ [3, 4] shows that the compound 2CaO.Fe$_2$O$_3$ dissociates at 1,436° C. prior to melting. Pure, finely ground CaCO$_3$ and Fe$_2$O$_3$ were thoroughly mixed in the correct proportions, bonded with a solution of gum and water and fired in an oxidising atmosphere to about 1,400° C., and slowly cooled. The material was crushed, bonded and re-fired, this process being repeated until a homogeneous product was obtained.

### 3CaO.Al$_2$O$_3$.

The binary system CaO–Al$_2$O$_3$ [5] shows that the compound 3CaO.Al$_2$O$_3$ melts incongruently at 1,535° C. Pure, finely ground CaCO$_3$ and Al$_2$O$_3$ in the correct proportions were thoroughly mixed, bonded and fired to 1,500° C. Crushing, bonding and firing were repeated until a homogeneous product was obtained.

### 5CaO.3Al$_2$O$_3$.

The binary diagram CaO–Al$_2$O$_3$ [5] shows that the compound 5CaO.3Al$_2$O$_3$ does not dissociate before melting. Pure, finely ground CaCO$_3$ and Al$_2$O$_3$ were thoroughly mixed in the correct proportions, bonded, and fired in a platinum crucible to the melting-point (1,455° C.). The material was maintained at this temperature for about 30 minutes and then slowly cooled.

The lime compounds, which served as standards, were proved to contain no free lime by means of White's test. Further, the X-ray photographs of these compounds were carefully examined for the patterns of the constituent oxides but, as can be observed, the pattern of each compound is quite characteristic, showing no trace of the constituent oxides. Pure samples of 3CaO.SiO$_2$, $\beta$-2CaO.SiO$_2$, $\gamma$-2CaO.SiO$_2$ and 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, supplied by the Building Research Station,[6] gave X-ray patterns identical with those prepared by the authors.

Periclase (MgO) has a cubic structure of the rock salt type, the lattice spacing being 4·20 Å. CaO has the same type of structure with the spacing of 4·80 Å. F. A. Steele and W. P. Davey [7] have reported that 3CaO.Al$_2$O$_3$ has a body-centred cubic structure with a complex unit cell, the lattice parameter being 3·18 Å. This spacing has been confirmed in the present work.

In contrast to these, the patterns of 3CaO.SiO$_2$, $\beta$-2CaO.SiO$_2$, $\gamma$-2CaO.SiO$_2$, 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$, 2CaO.Fe$_2$O$_3$ and 5CaO.3Al$_2$O$_3$ are much more complicated, consisting of a large number of lines. It may be noted that 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ and 2CaO.Fe$_2$O$_3$ have identical patterns except for a slight difference in spacing. Otherwise, each compound has a characteristic pattern which makes identification possible, even when a number of compounds occur together. Although 4CaO.Al$_2$O$_3$.Fe$_2$O$_3$ and 2CaO.Fe$_2$O$_3$ can be

readily distinguished from the other compounds, the similarity of their patterns makes it difficult to distinguish between them, although it is possible with careful measurement of the spacing. W. L. Hansen, L. T. Brownmiller and R. H. Bogue [8] reported complete solid solution between $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$. If dicalcium ferrite is considered as $4CaO.Fe_2O_3.Fe_2O_3$, the relation with $4CaO.Al_2O_3.Fe_2O_3$ becomes apparent. The probability of isomorphous substitution depends more upon ionic size than upon valency. The simplest case occurs when the ions are equal both in charge and size. The ionic radii of $Fe^{+++}$ and $Al^{+++}$ are 0·67 Å and 0·57 Å respectively.[9] Hence the Al and Fe ions are interchangeable in brownmillerite compositions. It is further interesting to note the similarity between the $Al_2O_3$ and $Fe_2O_3$ structures. These are rhombohedral with 2 molecules in the unit cell : $a=5·12$ Å, $\alpha=55°$ 17′ for $Al_2O_3$ and $a=5·42$ Å, $\alpha=55°$ 17′ for $Fe_2O_3$.[9] Partial solubility between $CaO.Fe_2O_3$ and $CaO.Al_2O_3$ is also known.

The X-ray photographs of the standards and a selection of the various series are shown in Figs. 12 to 17.

### QUANTITATIVE ESTIMATION OF CONSTITUENTS.

The relative intensities of reflection due to the different crystalline constituents in the mixture can serve as a measure of their relative amounts, but in attempting to apply this principle, it is essential to consider the difficulties inherent in the method which limit its scope. The authors have discussed these limitations and methods of minimising their effect elsewhere.[2] The aim is essentially to state (a) the presence or absence of a phase ; (b) whether it increases, decreases or remains constant ; (c) approximately the amount of each phase.

In the preliminary X-ray examination of the dolomite B—steatite A series,[2] the photographs plainly revealed the change of phases proceeding through the series. Photometer records also showed these tendencies very clearly. The same procedure was adopted in the present work. The photographs for each series clearly revealed the phases as tabulated in Table XVIII. A selection of the photometer curves which verified these results is given in Figs. 18 to 23. The same low angle range was chosen on each film, approximately 2 cm. in length, which contains characteristic lines of each phase. The range extended from A to B (Fig. 12). Records of the pure compounds are reproduced as reference standards. All photometer curves are so arranged that corresponding points are vertically aligned. With the information derived from the photographs and the photometer curves of the standards, the peaks in the photometer curves have been named according to the phase or phases they represent. Although each phase has a distinctive pattern, many reflections due to different constituents coincide, in particular those of $3CaO.SiO_2$, and $2CaO.SiO_2$. These coincident
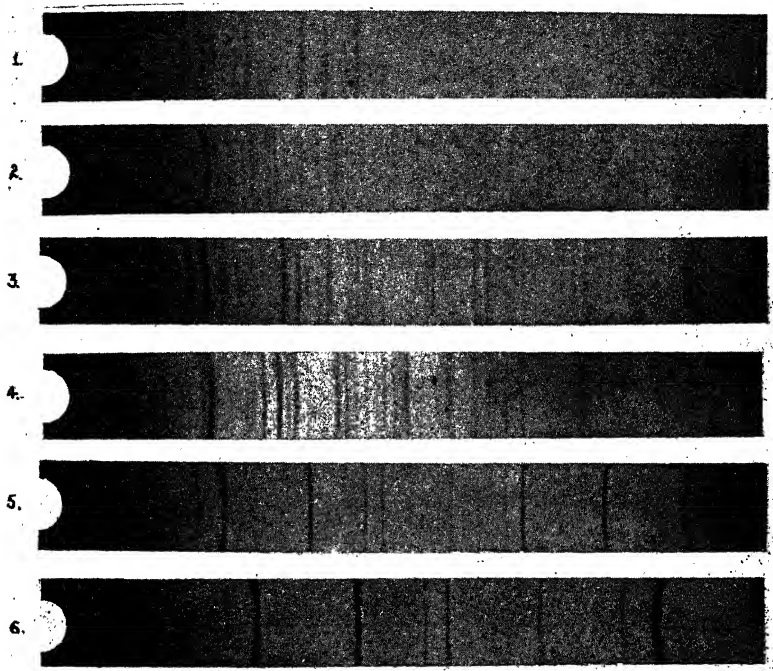
Fig. 12.—Powder X-ray photographs of reference materials.
Standards.

1. $3CaO.SiO_2$.
2. $\beta 2CaO.SiO_2$.
3. $\gamma 2CaO.SiO_2$.
4. $4CaO.Al_2O_3.Fe_2O_3$.
5. $CaO$.
6. $MgO$.

Figs. 13–17.—Powder X-ray photographs of fired dolomite mixtures.



Fig. 13.—Dolomite B—Flint.

1. 98 per cent. Dolomite B—2 per cent. Flint.
2. 96 per cent. Dolomite B—4 per cent. Flint.
3. 94 per cent. Dolomite B—6 per cent. Flint.
4. 92 per cent. Dolomite B—8 per cent. Flint.
5. 90 per cent. Dolomite B—10 per cent. Flint.
6. 88 per cent. Dolomite B—12 per cent. Flint.
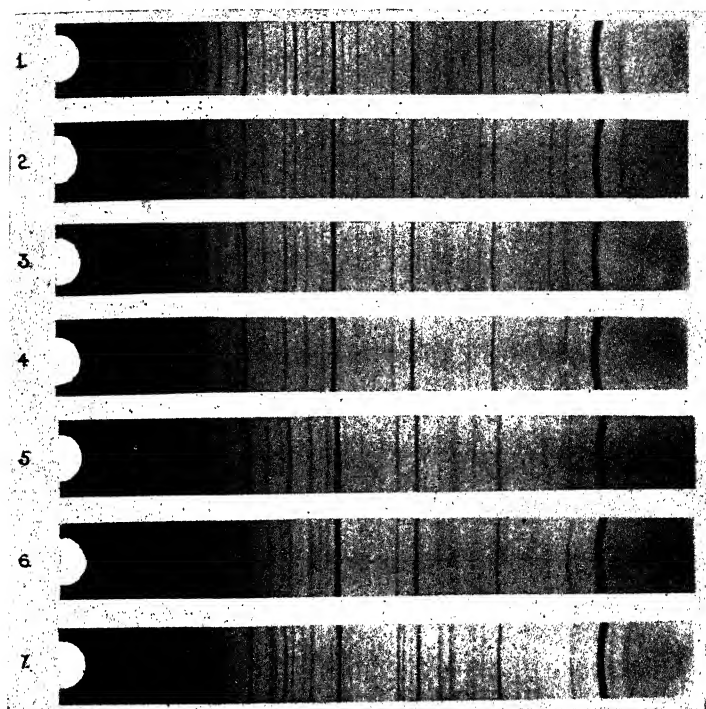
FIG. 14.—Dolomite A—Steatite F.G.X.O.

1. 85 per cent. Dolomite A—15 per cent. Steatite F.G.X.O.
2. 82 per cent. Dolomite A—18 per cent. Steatite F.G.X.O.
3. 80 per cent. Dolomite A—20 per cent. Steatite F.G.X.O.
4. 77 per cent. Dolomite A—23 per cent. Steatite F G X.O.
5. 75 per cent. Dolomite A—25 per cent. Steatite F.G.X.O.
6. 70 per cent. Dolomite A—30 per cent. Steatite F.G.X.O.
7. 65 per cent. Dolomite A—35 per cent. Steatite F.G.X.O.
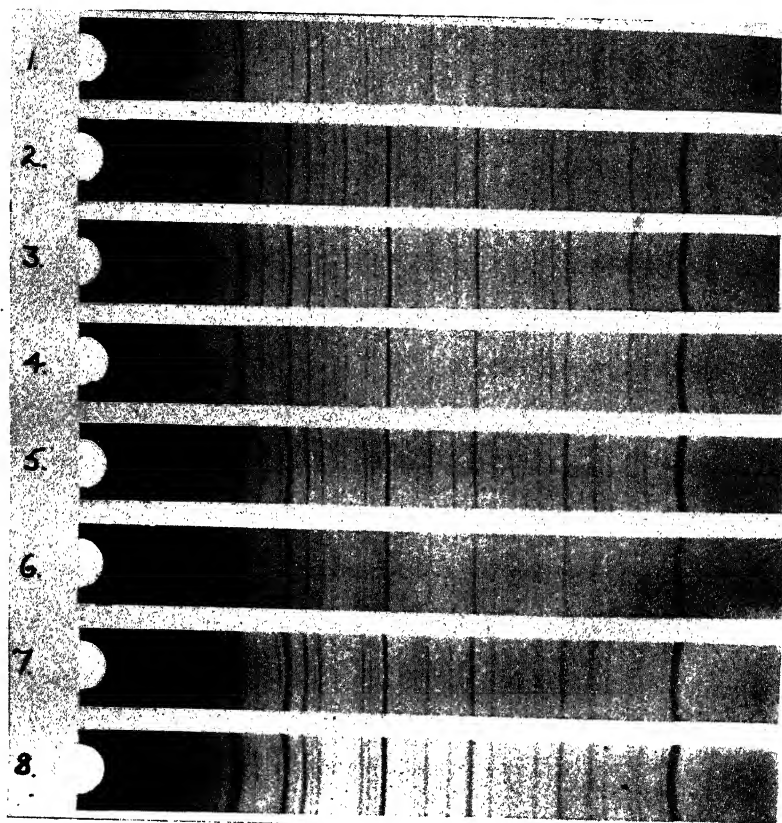
FIG. 15.—Dolomite B—$Fe_2O_3$.

1. $2\,CaO.Fe_2O_3$.
2. 90 per cent. Dolomite B—10 per cent. $Fe_2O_3$.
3. 88 per cent. Dolomite B—72 per cent. $Fe_2O_3$.
4. 86 per cent. Dolomite B—14 per cent. $Fe_2O_3$.
5. 84 per cent. Dolomite B—16 per cent. $Fe_2O_3$.
6. 82 per cent. Dolomite B—18 per cent. $Fe_2O_3$.
7. 80 per cent. Dolomite B—20 per cent. $Fe_2O_3$.
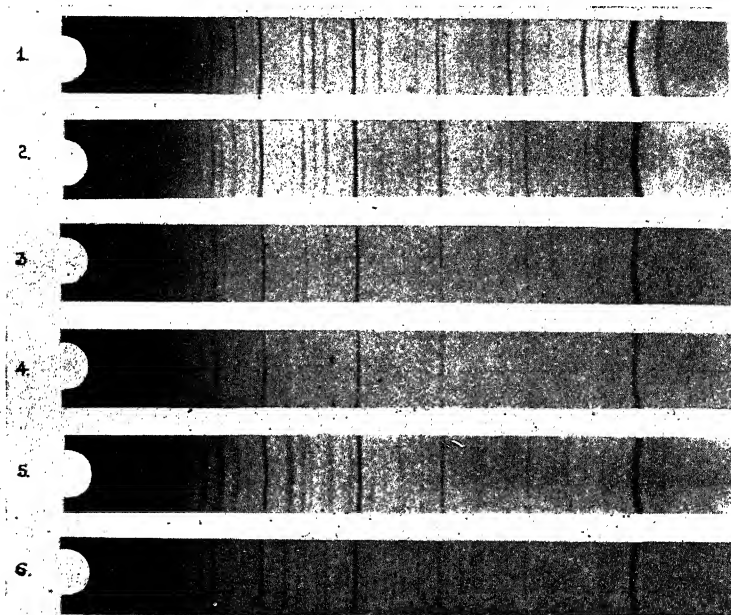8. 78 per cent. Dolomite B—22 per cent. $Fe_2O_3$.

FIG. 16.—Dolomite B—Bentonite.
1. 98 per cent. Dolomite B—2 per cent. Bentonite.
2. 96 per cent. Dolomite B—4 per cent. Bentonite.
3. 94 per cent. Dolomite B—6 per cent. Bentonite.
4. 92 per cent. Dolomite B—8 per cent. Bentonite.
5. 90 per cent. Dolomite B—10 per cent. Bentonite.
6. 88 per cent. Dolomite B—12 per cent. Bentonite.
7. 85 per cent. Dolomite B—15 per cent. Bentonite.
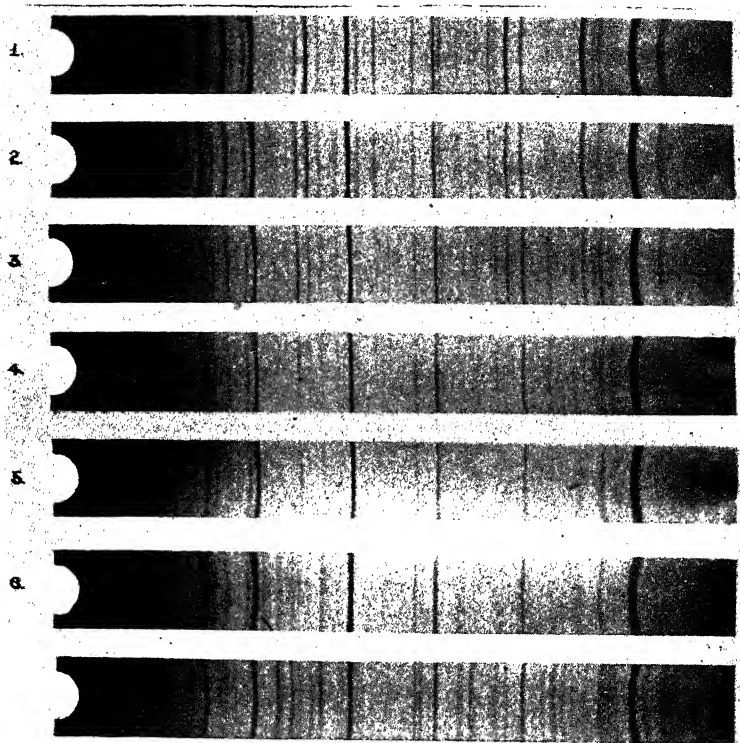
Fig. 17.—Dolomite B—$Al_2O_3$.

1. $3CaO.Al_2O_3$.
2. 96 per cent. Dolomite B—4 $Al_2O_3$.
3. 94 per cent. Dolomite B—6 per cent. $Al_2O_3$.
4. 92 per cent. Dolomite B—8 per cent. $Al_2O_3$.
5. 90 per cent. Dolomite B—10 per cent. $Al_2O_3$.
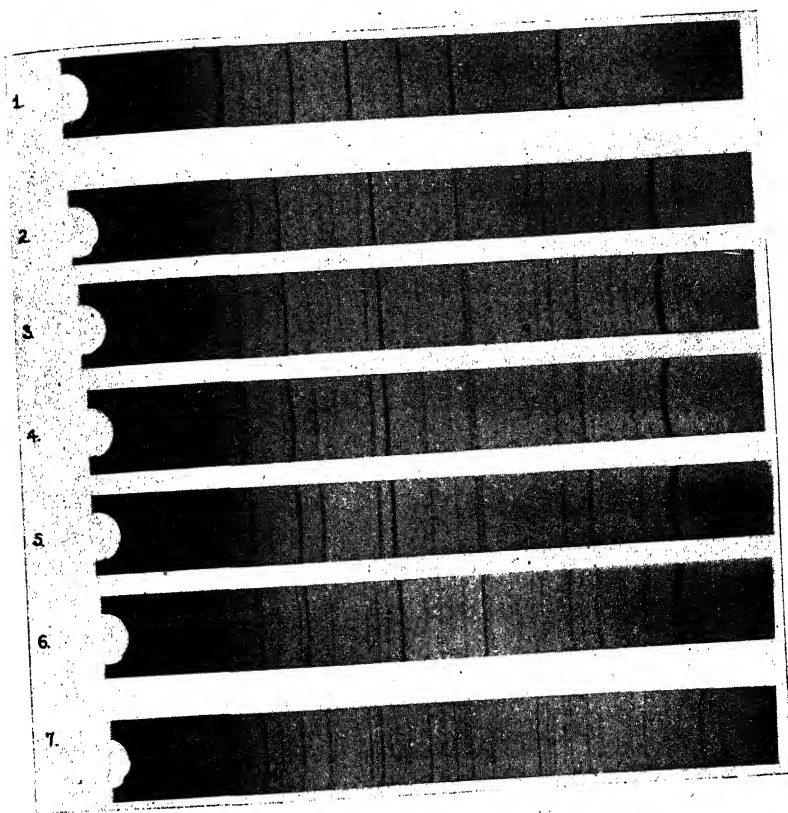6. 85 per cent. Dolomite B—15 per cent. $Al_2O_3$.
7. $5CaO.3Al_2O_3$.

lines are noted on the curves. Nevertheless, characteristic lines of each phase are present and can be used for comparison and even coincident lines can be employed for comparative purposes. In photometer curves of group 1, the strong reflection (200) of periclase is the most prominent, while lime is represented by two reflections (111) and (200) ; although the former coincides with a line of $3CaO.SiO_2$ and the latter with a line of periclase, they reveal the decreasing content of lime with increasing content of stabiliser. This decreasing content of lime is very clearly demonstrated by the high angle reflection shown in the photographs. The quantitative results are not merely obtained from the 2 cm. photometer records shown in Figs. 18 to 23, but from the records taken from the complete film. Since such records are too long to reproduce, the 2 cm. record is shown because it contains lines of each phase.

The results of the X-ray investigations are summarised in Table XVIII. Increasing amounts of a phase are indicated by arrows. In the case of $2CaO.SiO_2$ the arrows refer to the total of the $\beta$ and $\gamma$ forms. The calculated results obtained from a consideration of thermal equilibrium data [1] are also given for comparison.

DISCUSSION OF RESULTS.

A study of Table XVIII reveals that the X-ray findings are in complete accord with the results calculated on phase equilibria data.

The analysis of the series of group 1 shows that the clinkers consist chiefly of CaO, $SiO_2$, $Al_2O_3$, $Fe_2O_3$ and MgO. Hence the mineral constituents of all the mixes may be expressed by one of two five-component diagrams, depending on the $Al_2O_3/Fe_2O_3$ ratio. When the $Al_2O_3/Fe_2O_3$ ratio is greater than 102/160, the appropriate thermal diagram is $CaO–2CaO.SiO_2–5CaO.3Al_2O_3–4CaO.Al_2O_3.Fe_2O_3–MgO$. When the $Al_2O_3/Fe_2O_3$ ratio is less than 102/160, the appropriate diagram is $CaO–2CaO.SiO_2–4CaO.Al_2O_3.Fe_2O_3–2CaO.Fe_2O_3–MgO$. An exception is the dolomite-serpentine series which contains some $Cr_2O_3$. A six-component diagram would therefore be required to express the constitution, but since the percentage of $Cr_2O_3$ is low it is permissible to classify this series with the others. It is impossible to represent 5 component systems graphically, but it is possible to represent the various quaternary systems.

The quaternary phase diagrams related to the five-component diagram $CaO – 2CaO.SiO_2 – 5CaO.3Al_2O_3 – 4CaO.Al_2O_3.Fe_2O_3 – MgO$ are :—

A. $CaO–2CaO.SiO_2–5CaO.3Al_2O_3–MgO$.
B. $CaO–2CaO.SiO_2–5CaO.3Al_2O_3–4CaO.Al_2O_3.Fe_2O_3$.
C. $CaO–5CaO.3Al_2O_3–4CaO.Al_2O_3.Fe_2O_3–MgO$.
D. $CaO–2CaO.SiO_2–4CaO.Al_2O_3.Fe_2O_3–MgO$.
E. $MgO–5CaO.3Al_2O_3–4CaO.Al_2O_3.Fe_2O_3–2CaO.SiO_2$.

Figs. 18–23.—Photometer curves of region A to B (see Fig. 12) of X-ray photographs of fired dolomite mixtures: T–3CaO.SiO$_2$; L-CaO; M–MgO D$_1$–β-2CaO.SiO$_2$; D$_2$–γ-2CaO.SiO$_2$.
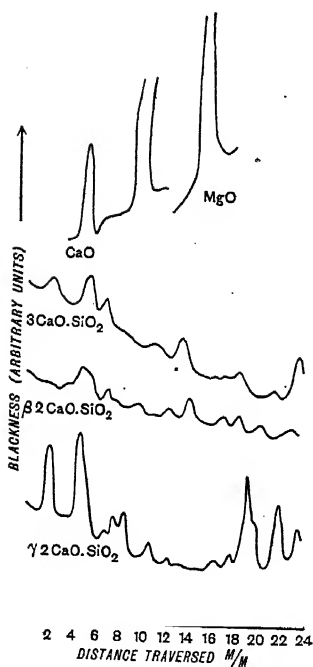


FIG. 18.—Standards.
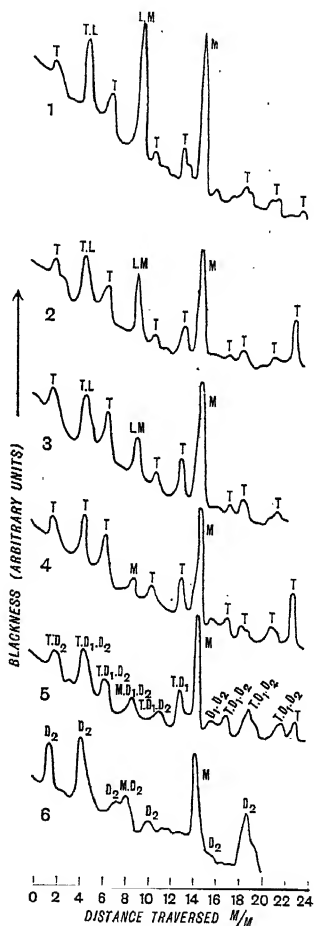
FIG. 19.—Dolomite B—Flint.

1. Dolomite B.
2. 2 per cent. Flint.
3. 4 per cent. Flint.
4. 6 per cent. Flint.
5. 8 per cent. Flint.
6. 10 per cent. Flint.
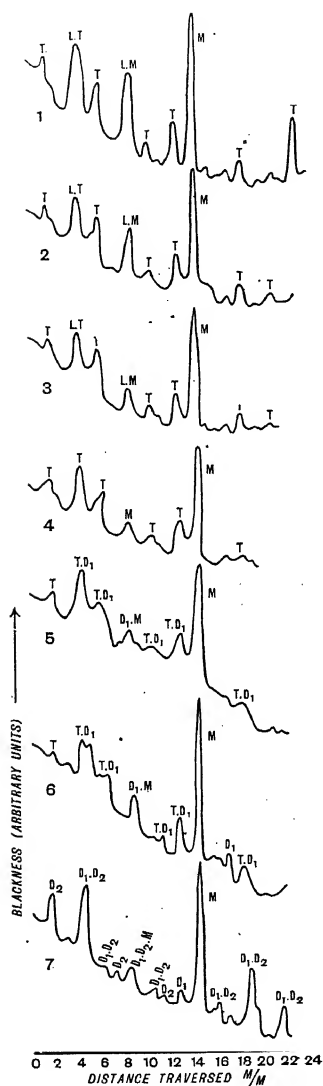
FIG. 20.—Dolomite B—Olivine.

1. 6 per cent. Olivine.
2. 8 per cent. Olivine.
3. 10 per cent. Olivine.
4. 12 per cent. Olivine.
5. 15 per cent. Olivine.
6. 17 per cent. Olivine.
7. 20 per cent. Olivine.
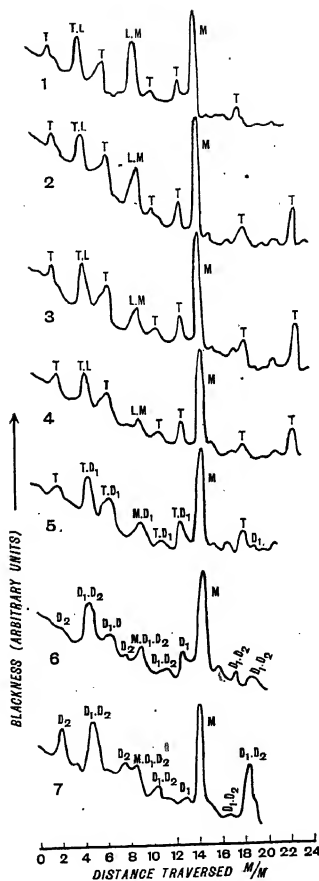
FIG. 21.—Dolomite B—Serpentine.

1. 5 per cent. Serpentine.
2. 7 per cent. Serpentine.
3. 10 per cent. Serpentine.
4. 12 per cent. Serpentine.
5. 15 per cent Serpentine
6. 20 per cent. Serpentine.
7. 23 per cent. Serpentine.

6

FIG. 22.—Dolomite B—China Clay.

1. 5 per cent. China Clay.
2. 7 per cent. China Clay.
3. 10 per cent. China Clay.
4. 12 per cent. China Clay.
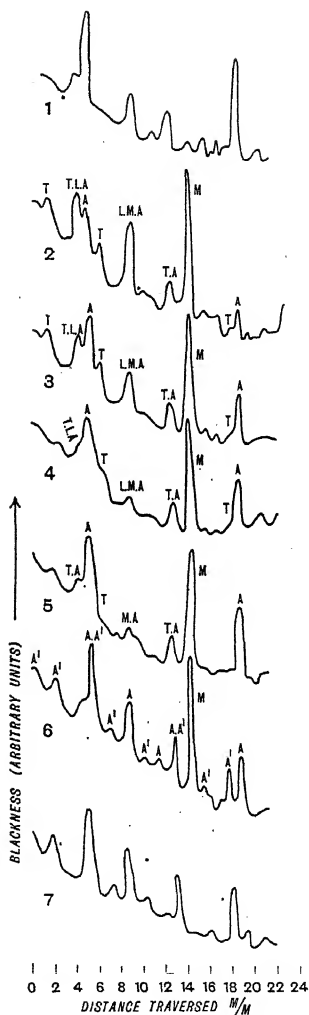
FIG. 23.—Dolomite B—Alumina.

1. 3CaO.Al$_2$O$_3$.
2. 4 per cent. Alumina.
3. 6 per cent. Alumina.
4. 8 per cent. Alumina.
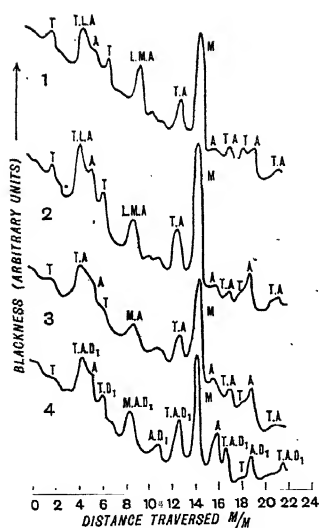5. 10 per cent. Alumina.
6. 15 per cent. Alumina.
7. 5CaO.3Al$_2$O$_3$

In the five-component system at equilibrium, the compounds which can coexist are :—

(1) $CaO$, $3CaO.SiO_2$, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and $MgO$.

(2) $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and $MgO$.

(3) $2CaO.SiO_2$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and $MgO$.

This has been verified by the present results. Previously F. M. Lea and T. W. Parker [6] had established the quaternary diagram $CaO$–$2CaO.SiO_2$–$4CaO.Al_2O_3.Fe_2O_3$–$5CaO.3Al_2O_3$, while H. F. McMurdie and H. Insley [10] had determined the quaternary $CaO$—$2CaO.SiO_2$–$5CaO.3Al_2O_3$–$MgO$. A study of the various ternary systems [11] indicated the form of the remaining quaternaries.

The quaternary phase diagrams related to the five-component diagram $CaO$ – $2CaO.SiO_2$ – $4CaO.Al_2O_3.Fe_2O_3$ – $2CaO.Fe_2O_3$ – $MgO$ are :—

D. $CaO$–$2CaO.SiO_2$–$4CaO.Al_2O_3.Fe_2O_3$–$MgO$.

F. $CaO$–$2CaO.SiO_2$–$4CaO.Al_2O_3.Fe_2O_3$–$2CaO.Fe_2O_3$.

G. $CaO$–$2CaO.SiO_2$–$2CaO.Fe_2O_3$–$MgO$.

H. $CaO$–$4CaO.Al_2O_3.Fe_2O_3$–$2CaO.Fe_2O_3$–$MgO$.

I. $MgO$–$4CaO.Al_2O_3.Fe_2O_3$–$2CaO.Fe_2O_3$–$2CaO.SiO_2$.

In the five-component system at equilibrium, the compounds which can coexist are :—

(1) $CaO$, $3CaO.SiO_2$, $2CaO.Fe_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and $MgO$.

(2) $3CaO.SiO_2$, $2CaO.SiO_2$, $2CaO.Fe_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$ and $MgO$.

These conclusions have been verified by the present results.

These latter quaternary diagrams have not been previously established, but the various appropriate ternary diagrams [11] provided a fairly accurate indication of the possible quaternary and five-component phase diagrams.

$2CaO.Fe_2O_3$ and $4CaO.Al_2O_3.Fe_2O_3$ are mutually soluble in all proportions,[8] so that when these occur they will be in solid solution, and only one phase will be visible under the microscope or indicated by X-rays. No appreciable amount of solid solution can exist between the other compounds, since it would show up in the X-ray patterns as a progressive shift in the lines. Careful measurements of the patterns revealed no shift in the lines. I. Weyer [12] burnt mixes of $3CaO.SiO_2$ and $3CaO.Al_2O_3$ and examined them optically and by X-rays. He concluded that $3CaO.SiO_2$ takes up practically no alumina into solid solution. Recent work [13] has definitely shown that tricalcium silicate can take up in solid solution small amounts of other oxides. Thus this compound has been obtained containing 2·01 per cent. $FeO$, 0·76 per cent. $Fe_2O_3$, 1·20 per cent. $MnO$, 1·29 per cent. $MgO$, 0·18 per cent. $TiO_2$, and 0·20 per cent. $Al_2O_3$, of which the greater part was in solid solution, the remainder being present as discrete particles of impurities. While such small

TABLE XVIII.—DATA ON THE CONSTITUTION OF DOLOMITE CLINKERS.

| Group (See Fig. 25 and Table XIX). | Dolomite per cent. | Stabiliser per cent. | Mineralogical Constitution as determined by X-rays. | | | | | | Calculated Mineralogical Composition (weight per cent.) | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | Free CaO. | $3CaO.SiO_2$. | $\beta\text{-}2CaO.SiO_2$. | $\gamma\text{-}2CaO.SiO_2$. | Periclase (MgO). | $2CaO.Fe_2O_3$-$4CaO.Al_2O_3.Fe_2O_3$ solid solution. | Periclase (MgO). | Free CaO. | $3CaO.SiO_2$. | $4CaO.Al_2O_3.Fe_2O_3$. | $3CaO.Al_2O_3$. | $5CaO.3Al_2O_3$. | $2CaO.SiO_2$. | $2CaO.Fe_2O_3$. | $2CaO.Cr_2O_3$. |
| A | B 100 | 0 | P | P | — | — | P | — | 36·0 | 29·6 | 26·4 | 5·4 | 1·7 | — | — | — | — |
| A | B 98 | Flint 2 | P | P | — | — | P | — | 34·7 | 18·9 | 38·7 | 5·2 | 1·7 | — | — | — | — |
| C | 96 | 4 | P ← | P → | — | — | P | — | 33·5 | 8·4 | 50·7 | 5·0 | 1·6 | — | — | — | — |
| D | 94·3 | 5·7 | — | P max | — | — | P | — | 32·5 | — | 59·2 | 4·8 | 1·6 | — | 1·0 | — | — |
| F | 92 | 8 | — | P | P → | P | P | — | 31·1 | — | 26·1 | 4·6 | 1·5 | — | 35·7 | — | — |
| G | 90 | 10 | — | — | → | P | P | — | 30·0 | — | — | 4·5 | — | 1·1 | 63·0 | — | — |
| A | B 95 | Steatite A.T.1 5 | P | P | — | — | P | — | 36·4 | 18·1 | 37·0 | 6·7 | 0·9 | — | — | — | — |
| B | 90 | 10 | P ← | P → | — | — | P | — | 36·7 | 7·0 | 47·0 | 8·0 | 0·3 | — | — | — | — |
| D | 88 | 12 | Tr | P max | — | — | P | — | 36·9 | 2·7 | 51·0 | 8·4 | — | — | — | — | — |
| E | 85 | 15 | — | P | — | — | P | — | 37·1 | — | 42·3 | 8·4 | — | — | 10·9 | 0·5 | — |
| F | 83 | 17 | — | P | P → | — | P | — | 37·3 | — | 29·5 | 8·4 | · | — | 22·9 | 0·8 | — |
| G | 80 | 20 | — | — | → | P | P | — | 37·4 | — | 8·5 | 8·4 | — | — | 43·5 | 1·1 | — |
| A | B 95 | Steatite F.G.X.O. 5 | P | P | — | — | P | — | 35·9 | 17·4 | 37·3 | 6·9 | 1·7 | — | — | — | — |
| B | 93 | 7 | P ← | P → | — | — | P | — | 35·9 | 12·7 | 41·5 | 7·5 | 1·7 | — | — | — | — |
| C | 90 | 10 | P | P max | — | — | P | — | 35·8 | 5·8 | 47·6 | 8·4 | 1·6 | — | — | — | — |
| D | 88 | 12 | Tr | P | — | — | P | — | 35·8 | 1·2 | 51·6 | 8·9 | 1·6 | — | — | — | — |
| E | 85 | 15 | — | P | P → | — | P | — | 35·8 | — | 35·5 | 9·8 | 1·6 | — | 16·6 | — | — |
| G | 80 | 20 | — | — | → | P | P | — | 35·7 | — | 1·8 | 11·1 | 1·5 | — | 49·1 | — | — |

### Olivine series

| | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| | — | — | — | — | — | — | — |
| | — | — | — | — | — | — | 0·2 |
| | — | — | — | — | 18·5 | 31·6 | 48·3 |
| | — | — | — | — | — | — | — |
| | 1·1 | 1·0 | 0·7 | 0·6 | 0·3 | 0·1 | — |
| | 6·7 | 7·2 | 7·6 | 8·0 | 8·6 | 8·9 | 9·2 |
| | 39·3 | 44·6 | 47·7 | 51·6 | 32·7 | 19·0 | — |
| | 14·5 | 8·9 | 5·0 | 0·1 | — | — | — |
| | 37·4 | 37·9 | 38·3 | 38·7 | 39·3 | 39·7 | 40·3 |
| | — | — | — | — | — | — | — |
| | P | P | P | P | P | P | P |
| | — | — | — | — | — | — | P |
| | — | — | — | — | P→ | P→ | |
| | P | P | P | P max | P | Tr | — |
| | P | P | P | — | — | — | — |
| Olivine | 6 | 8 | 10 | 12 | 15 | 17 | 20 |
| B | 94 | 92 | 90 | 88 | 85 | 83 | 80 |

### Serpentine series

| | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| | 1·0 | 1·3 | 1·8 | 2·2 | 2·7 | 3·5 | |
| | — | — | — | — | 0·4 | 1·1 | |
| | — | — | — | — | 4·9 | 35·2 | |
| | — | — | — | — | — | — | — |
| | 1·0 | 0·7 | 0·3 | — | — | | |
| | 7·6 | 8·5 | 9·7 | 10·6 | 10·8 | 11·8 | |
| | 34·7 | 37·9 | 42·7 | 45·6 | 43·5 | 10·4 | |
| | 18·6 | 14·4 | 8·2 | 4·1 | — | | |
| | 36·3 | 36·6 | 36·7 | 36·8 | 37·0 | 37·3 | |
| | — | — | — | — | — | — | |
| | P | P | P | P | P | P | |
| | — | — | — | — | Tr | P | |
| | — | — | — | P→ | P→ | | |
| | P | P | P | P max | Tr | — | |
| | P | P | Tr | — | — | — | |
| Serpentine | 5 | 7 | 10 | 12 | 15 | 20 | 23 |
| B | 95 | 93 | 90 | 88 | 85 | 80 | 77 |

### Steatite F.G.X.O. series

| | A | B | C | D | E | F | G |
|---|---|---|---|---|---|---|---|
| | — | — | — | — | — | — | |
| | 2·1 | 2·0 | 2·0 | 1·9 | 1·8 | 1·6 | |
| | — | — | — | — | 0·1 | 26·1 | |
| | — | — | — | — | — | — | |
| | — | — | — | — | — | — | |
| | 8·4 | 9·1 | 9·5 | 10·2 | 10·6 | 11·7 | |
| | 35·1 | 40·2 | 42·6 | 47·1 | 50·1 | 23·3 | |
| | 16·2 | 11·1 | 8·3 | 3·3 | — | | |
| | 37·1 | 37·0 | 37·0 | 36·9 | 36·8 | 36·6 | |
| | Tr | Tr | P | P | P | — | |
| | P | P | P | P | P | P | |
| | — | — | — | — | — | P | |
| | — | — | — | — | P→ | P | |
| | P | P | P | P max | P | ← | |
| | P | P | P | Tr | — | — | |
| Steatite | 15 | 18 | 20 | 23 | 25 | 30 | 35 |
| A | 85 | 82 | 80 | 77 | 75 | 70 | 65 |

### Ferric oxide series

| | A | B | C | D | E | F |
|---|---|---|---|---|---|---|
| | — | — | — | — | — | — |
| | 26·9 | 32·1 | 37·2 | 42·1 | 46·9 | 51·6 |
| | — | — | — | — | — | 3·1 |
| | — | — | — | — | — | — |
| | — | — | — | — | — | — |
| | 7·1 | 6·8 | 6·6 | 6·3 | 6·1 | 5·8 |
| | 22·0 | 21·2 | 20·4 | 19·7 | 18·9 | 14·2 |
| | 12·8 | 10·3 | 7·4 | 4·6 | 1·7 | — |
| | 30·0 | 28·9 | 27·8 | 26·8 | 25·9 | 24·8 |
| | P | P | P | P | P→ | |
| | P | P | P | P | P | |
| | — | — | — | — | — | — |
| | — | — | — | — | — | — |
| | ← | P | P | P | P | P |
| | P | P | P | P | — | — |
| Ferric oxide | 10 | 12 | 14 | 16 | 18 | 20 |
| B | 90 | 88 | 86 | 84 | 82 | 80 |

TABLE XVIII.—continued.

| Dolomite per cent. | Stabiliser per cent. | Mineralogical Constitution as determined by X-rays. | | | | | | | Calculated Mineralogical Composition (weight per cent.). | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Free CaO. | $3CaO.SiO_2$. | $\beta$-$2CaO.SiO_2$. | $\gamma$-$2CaO.SiO_2$. | Periclase (MgO). | $3CaO.Al_2O_3$. | $5CaO.3Al_2O_3$. | Periclase (MgO). | Free CaO. | $3CaO.SiO_2$. | $4CaO.Al_2O_3.Fe_2O_3$. | $3CaO.Al_2O_3$. | $5CaO.3Al_2O_3$. | $2CaO.SiO_2$. | $2CaO.Fe_2O_3$. |
| | *Steatite* | | | | | | | | | | | | | | | |
| B | 3B | | | | | | | | | | | | | | | |
| 95 | 5 | P | P | | | P | Tr | | 35·7 | 14·5 | 39·6 | 5·5 | 3·8 | | | |
| 90 | 10 | Tr | P max | | | P | P | | 35·5 | 0·3 | 52·0 | 5·6 | 5·6 | | 16·0 | |
| 88 | 12 | | P | P | | P | P | | 35·4 | | 35·5 | 5·6 | 6·4 | | 37·5 | |
| 85 | 15 | | P | P | | P | P | | 35·3 | | 13·9 | 5·7 | 7·5 | | 51·4 | |
| 83 | 17 | | | | P | P | | | 35·2 | | | 5·7 | 2·4 | 4·2 | | |
| | *Bentonite* | | | | | | | | | | | | | | | |
| B | | | | | | | | | | | | | | | | |
| 98 | 2 | P | P | | | P | Tr | | 35·0 | 22·5 | 32·8 | 5·6 | 3·2 | | | |
| 96 | 4 | P | P | | | P | P | | 34·1 | 15·3 | 39·1 | 5·7 | 4·7 | | | |
| 94 | 6 | P | P | | | P | P | | 33·2 | 8·4 | 45·2 | 5·9 | 6·1 | | | |
| 92 | 8 | Tr | P max | | | P | P | | 32·3 | 1·7 | 51·3 | 6·3 | 7·5 | | | |
| 90 | 10 | | P | | | P | P | | 31·4 | | 35·9 | 6·3 | 9·0 | | 16·1 | |
| 88 | 12 | | P | Tr | | P | Tr | | 30·5 | | 15·4 | 6·5 | 10·3 | | 34·8 | |
| 85 | 15 | | | P | P | P | | | 29·2 | | | 6·7 | | 9·0 | 51·7 | |

| | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **China Clay** | | | | | | | | | | | | | | |
| B — 5 | P← | P | | | P | P | | 33·3 | 10·4 | 40·0 | 5·1 | 8·2 | | | |
| 96 — 7 | P | P max | | | P | P | | 32·2 | 3·0 | 45·2 | 5·0 | 13·8 | | | |
| 93 — 10 | | | P→ | | P | P | | 30·7 | | 20·7 | 4·8 | 18·7 | | 24·2 | |
| 90 — 12 | | | P | | P | | | 29·7 | | — | 4·7 | 19·4 | 1·8 | 43·5 | |
| 88 — 15 | | | | P | P | | | | | | | | | | |
| 85 | | | | | | | | | | | | | | | |
| **Alumina** | | | | | | | | | | | | | | |
| B — 4 | P← | P← | | | P | P | | 33·5 | 16·1 | 24·6 | 5·0 | 20·1 | | | |
| 96 — 6 | P | P | | | P | P | | 32·3 | 9·6 | 23·7 | 4·8 | 28·8 | | | |
| 94 — 8 | Tr | P | | | P | P→ | | 31·1 | 3·4 | 22·8 | 4·7 | 37·3 | | | |
| 92 — 10 | | Tr | | | P | P max↑ | | 30·0 | | 11·0 | 4·5 | 45·6 | 32·1 | 8·3 | |
| 90 — 15 | | | | | P | P | P | 27·3 | | — | 4·1 | 20·8 | | 15·1 | |
| 85 | | | | | | | | | | | | | | | |

P indicates the presence of the compound.

Tr indicates the presence of a trace of the compound.

P max indicates the presence of the maximum amount of the compound in the series.

amounts of solid solution do not alter appreciably the optical properties of tricalcium silicate, F. M. Lea and C. H. Desch [14] suggest that they may affect the reactivity of the material to water and that valuable information may be obtained by studies along such lines.

The visibility limit of the X-ray powder method in detecting compounds was discussed in Part II.[2]   The pattern obtained from an X-ray photograph of a crystalline substance consists of lines of varying intensity.   It has been shown that in the dolomite mixtures, some of the lines due to the various compounds present nearly coincide.   As the quantity of one of the crystalline materials present decreases, the general intensity of the pattern due to it decreases, until ultimately a point is reached when even its most intense lines can no longer be detected.   The minimum quantity of a crystalline substance which can be detected by X-ray diffraction methods in a mixture depends therefore on the intensity of its strongest lines, and the degree to which their positions differ from lines due to other compounds present.   In general, crystalline materials belonging to the crystallographic systems of higher symmetry, such as the cubic, tend to give strong patterns containing relatively few lines, while materials of lower crystal symmetry give weaker patterns and a great number of lines.   According to F. M. Lea and C. H. Desch,[14] tricalcium silicate belongs to the trigonal system, but dicalcium silicate is of lower symmetry.   The former gives a pattern containing some fairly strong lines, but the $\beta$-dicalcium silicate pattern contains many weak lines and its strongest lines are close to the strong lines of the tricalcium silicate.   This may be observed in Fig. 12.   The identification of $\beta$-dicalcium silicate in presence of tricalcium silicate is therefore uncertain unless a fairly large amount of it, about 15 per cent., is present.

· L. T. Brownmiller and R. H. Bogue [15] have concluded from a study of a series of cement clinkers prepared in the laboratory that the minimum amounts of the various possible compounds which must be present to be susceptible to identification by X-ray diffraction methods are as follows : 8 per cent. $3CaO.SiO_2$ ; 15 per cent. $\beta$-$2CaO.SiO_2$ ; 6 per cent. $3CaO.Al_2O_3$ ; 15 per cent. $4CaO.$ $Al_2O_3.Fe_2O_3$ ; 2·5 per cent. MgO ; 2·5 per cent. CaO.

L. T. Brownmiller and R. H. Bogue [15] examined many commercial cement clinkers.   Three were of such analytical composition that, assuming equilibrium to be established, the contents of the compounds present would be as follows :—

|  | (1) | (2) | (3) |
|---|---|---|---|
| $3CaO.SiO_2$ .. .. | 37 | 41 | 50 |
| $2CaO.SiO_2$ .. .. | 38 | 35 | 31 |
| $3CaO.Al_2O_3$ .. | 13 | 13 | 3 |
| $4CaO.Al_2O_3.Fe_2O_3$ | 8 | 7 | 15 |
| MgO .. .. | 4·1 | 3·1 | 0·6 |
| Free CaO .. | 0 | 0·4 | 0 |

The X-ray method showed· the presence of $3CaO.SiO_2$ and

$2CaO.SiO_2$ in all three.   In (1) and (2) $3CaO.Al_2O_3$ and MgO were also found, but no $4CaO.Al_2O_3.Fe_2O_3$ lines could be found.   The lines of $4CaO.Al_2O_3.Fe_2O_3$ in addition to those of the silicates could be identified in (3) only.   The amounts present of $4CaO.Al_2O_3.$ $Fe_2O_3$ in (1) and (2) and MgO and $3CaO.Al_2O_3$ in (3) were below the limits necessary for identification.

Of twenty-eight cement clinkers examined by L. T. Brown-miller and R. H. Bogue, $3CaO.SiO_2$ and $\beta$-$2CaO.SiO_2$ were identified in all, and furthermore their patterns were always the most prominent, indicating that they were the more abundant constituents. One or more of the compounds $3CaO.Al_2O_3$, $4CaO.Al_2O_3.Fe_2O_3$, and MgO were identified in most of the clinkers, but not all these latter compounds were identified in all clinkers.   F. M. Lea and C. H. Desch [14] have concluded that these results, together with the data from phase equilibria, the results of optical examination and of chemical analysis, form fairly conclusive evidence for the constitution of portland cement.   Portland cement is prepared by burning mixtures of limestone and clay in suitable proportion in a rotary kiln.   Chemical analysis of the clinker shows it to consist chiefly of CaO, $SiO_2$, $Al_2O_3$, $Fe_2O_3$ and MgO.   The chief difference between portland cement and stabilised dolomite clinker is that the MgO content is much lower in the former, rarely exceeding 5 per cent. The constitutions calculated on the basis of the phase diagrams discussed on page 73 agree with the X-ray and microscope findings. This provides additional evidence of the validity of these diagrams.

It was previously emphasized that no one method of approach to the complicated problem of the constitution of dolomite clinkers may be regarded of itself as altogether conclusive.[2]   The X-ray method by itself is inconclusive because of its limitations in detecting small amounts of phases.   Thus, examination of a typical dolomite clinker, which by calculation contains 40·7 per cent. MgO, 18·0 per cent. $3CaO.SiO_2$, 32·1 per cent. $2CaO.SiO_2$, 4·9 per cent. $4CaO.Al_2O_3.Fe_2O_3$ and 3·4 per cent. $2CaO.Fe_2O_3$, would reveal the patterns of MgO, $3CaO.SiO_2$ and $2CaO.SiO_2$, but would not reveal the presence of $4CaO.Al_2O_3.Fe_2O_3$ and $2CaO.Fe_2O_3$, because the amounts are below the limit of visibility.   The intimate intergrowth of the crysta l phases militates against their separation based on differences in specific gravity.   Petrological microscope studies are probably satisfactory on specially prepared laboratory clinkers, but the fineness of the crystals of commercially prepared dolomite clinkers makes such a study difficult.   The presence of the minor phases in dolomite clinkers is therefore indicated solely by phase equilibrium calculations.

A further indication of the validity of the phase equilibrium calculations was obtained by examination of the X-ray photographs in the following way.

Table XVIII shows that a large number of the clinkers examined have a very low content of calcium aluminates and dicalcium ferrite.

Hence it was permissible to represent their constitution in a quaternary space model of the $CaO-2CaO.SiO_2-4CaO.Al_2O_3.Fe_2O_3-MgO$ system. The points are crowded into a very narrow strip (Fig. 24) and it is difficult to follow the individual points clearly on a photograph. Moreover, the $4CaO.Al_2O_3.Fe_2O_3$ present in all the compositions plotted was below the X-ray visibility limit, therefore the $4CaO.Al_2O_3.Fe_2O_3$ content has been neglected and the composition of the remaining constituents calculated to 100 per cent. These compositions have been plotted on a ternary diagram $CaO-2CaO.SiO_2-MgO$ as shown in Fig. 25. Since the $4CaO.Al_2O_3.Fe_2O_3$ content does not vary greatly, the error introduced is small. The
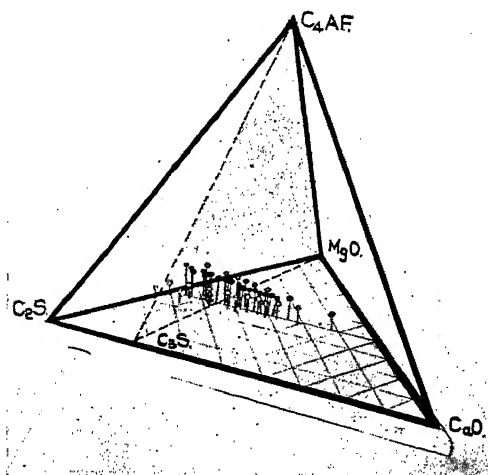


Fig. 24.—Space model showing the variation of the constitution of dolomite clinkers with increasing amounts of stabiliser.

X-ray photographs were classified into groups. In each group, the members showed similar phase constituents both qualitatively and quantitatively. Each clinker has been given a letter according to its X-ray group (see Table XVIII) and, as can be seen in Fig. 25, the X-ray classification agrees closely with the calculated results. The key to the classification into groups approximately alike, according to the X-ray results, is as given in Table XIX.

The dolomite clinkers which have been the subject of this investigation were prepared by sintering the raw materials, which had been finely ground and intimately mixed, at a temperature such that only a portion of the material would be liquid.

Now, chemical reactions between solid substances, even when they are intimately mixed, tend to proceed only slowly, and it has

TABLE XIX.—X-RAY CLASSIFICATION OF DOLOMITE CLINKERS.

| Group. | Free Lime. | $3CaO.SiO_2$. | $2CaO.SiO_2$. | MgO. |
|--------|-----------|----------------|----------------|------|
| A | Large | Medium/small | Absent | Large |
| B | Medium | Medium | ,, | ,, |
| C | Small | Large/medium | ,, | ,, |
| D | Absent. | Large | ,, | ,, |
| E | ,, | Large/medium | $\beta$ Present | ,, |
| F | ,, | Medium/small | More $\beta$, trace $\gamma$ | ,, |
| G | ,, | Absent | Large $\gamma$ | ,, |
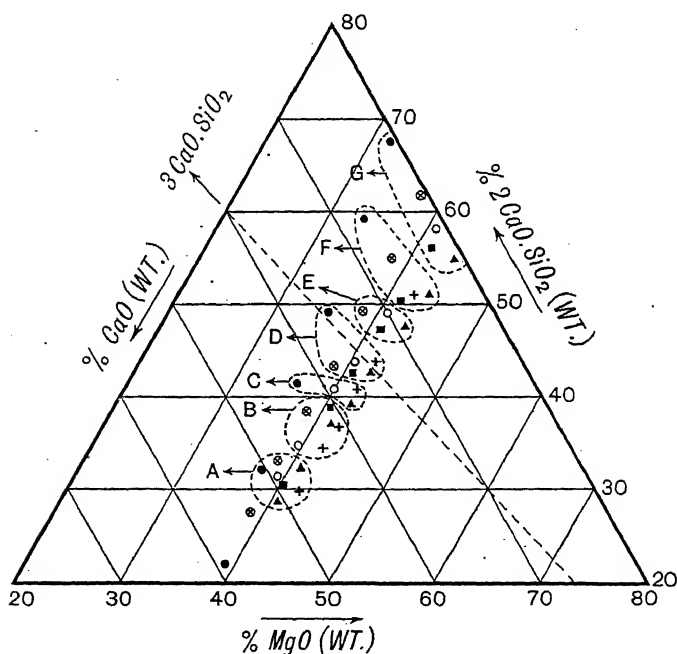


Fig. 25.—Relation between constitution of dolomite clinkers as indicated by X-ray analysis and approximate constitution as indicated by position no the $2CaO.SiO_2$–CaO–MgO diagram.

A, B, C, D, E, F, G.    (See Table XIX.)

● Dolomite B and O, 2, 4, 5·7, 8, and 10 per cent. Flint mixtures.

■ Dolomite B and 5, 10, 12, 15, 17 and 20 per cent. Steatite A.T.I. mixtures.

○ Dolomite B and 5, 7, 10, 12, 15 and 20 per cent. Steatite F.G.X.O. mixtures.

▲ Dolomite B and 4, 6, 8, 10, 12, 15, 17 and 20 per cent. Olivine mixtures.

⊗ Dolomite B and 2, 4, 6, 8, 10, 12 and 15 per cent. Steatite A mixtures.

+ Dolomite A and 15, 18, 20, 23, 25 and 30 per cent. Steatite F.G.X.O. mixtures.

been usually considered that, under such conditions, equilibrium would not be approached.

F. M. Lea and C. H. Desch [14] have discussed two ways in which clinkers prepared by sintering might depart from the equilibrium state. The reactions during the firing of the raw dolomite and stabiliser may form the normal compounds to be expected from the phase equilibrium diagrams, but, owing to their sluggishness, these reactions might not be quite complete. The result would be a decrease in the amounts of the most basic compounds formed, particularly tricalcium silicate. An increase in the firing time or temperature would result in a closer approach to equilibrium. Such quantitative departures from equilibrium would only change the properties of the clinker in so far as free lime affected it, since all the other compounds present would be the normal equilibrium compounds, though their proportions would be somewhat changed. Another possible departure from equilibrium which suggests itself is that, during the firing, unstable compounds are formed which differ from the equilibrium compounds and which never occur in studies on systems in equilibrium. These unstable compounds would be low in lime, which would tend to leave uncombined lime in the clinkers.

The hydration curves,[1] free lime analysis,[2] and X-ray diffraction photographs give fairly conclusive evidence that the equilibrium state is reached. The similarity of the X-ray photographs of the various clinkers which phase equilibrium calculations indicated as having similar constitutions is very striking, especially as the clinkers were prepared with different stabilisers.

Do the same principles apply to commercially prepared dolomite clinkers ? Stabilised clinker is prepared by sintering the finely ground dolomite intimately mixed with a suitable proportion of finely ground stabiliser in a rotary kiln at a temperature such that only a portion of the material becomes liquid. Since at the highest temperature, some liquid is formed and the drop in temperature in passing from the hot zone is rapid, the equilibrium conditions at high temperatures will tend to be maintained at room temperatures. In other words, a certain amount of glassy material, which has not had sufficient time to crystallise, will occur in the clinker. Since the equilibrium conditions of the appropriate five-component systems are not known in detail, it is not yet possible to calculate the amount of glass formed. Hence, calculations based on phase equilibrium at room temperatures would not be strictly accurate. However, F. M. Lea and C. H. Desch [14] have considered the somewhat analogous case of portland cement which will be briefly discussed, for it has a bearing on the amount of glass to be expected in the dolomite clinkers. As previously mentioned, portland cement clinker is made from lime and clay in a rotary kiln in a similar manner to dolomite clinker. On passing from the hot zone there is a rapid fall in temperature, so that there is not

sufficient time for complete crystallisation. Hence there is a certain amount of glassy material in the cement clinker, depending upon the composition, temperature and time of burning and the rate of fall in temperature in passing from the hot zone. F. M. Lea and C. H. Desch [14] have stated: " Essentially, then, we can regard portland cement clinker as a material which has approached equilibrium at the clinkering temperatures, but which has cooled too rapidly for all the liquid to crystallise and complete equilibrium to be established at the temperature of final solidification." Thus the relative proportions of the compounds present will differ somewhat from that calculated from the composition. Since the constitution of portland cement can be more or less expressed by the quarternary diagram $CaO–2CaO.SiO_2–5CaO.3Al_2O_3–4CaO.Al_2O_3.Fe_2O_3$, which has been investigated in detail,[6] F. M. Lea and C. H. Desch [14] have been able to calculate the changes in constitution due to glass formation. This is illustrated by the data in Table XX, where the compound contents of two cements

TABLE XX.—CHANGES IN CONSTITUTION DUE TO GLASS FORMATION OF TWO CEMENT CLINKERS (F. M. LEA AND C. H. DESCH).

| | Complete crystallisation. | 1,450° C. Liquid quenched to glass. | 1,450° C. Liquid crystallises independently. |
|---|---|---|---|
| Cement composition (per cent.): $CaO=68$ ; $SiO_2=23$ ; $Al_2O_3=7$ | | | |
| $3CaO.SiO_2$ .. .. | 52·2 | 59·4 | 59·4 |
| $2CaO.SiO_2$ .. .. | 26·5 | 15·3 | 21·4 |
| $3CaO.Al_2O_3$ .. | 15·2 | 0 | 9·7 |
| $4CaO.Al_2O_3.Fe_2O_3$ | 6·1 | 0 | 5·9 |
| Free CaO .. | 0 | 0 | 0 |
| $5CaO.3Al_2O_3$ .. | 0 | 0 | 3·8 |
| Glass .. .. | 0 | 25·5 | 0 |
| Cement composition (per cent.): $CaO=67$ ; $SiO_2=23$ ; $Al_2O_3=4$ ; $Fe_2O_3=6$. | | | |
| $3CaO.SiO_2$ .. .. | 62·7 | 55·1 | 61·3 |
| $2CaO.SiO_2$ .. .. | 18·6 | 19·4 | 19·4 |
| $3CaO.Al_2O_3$ .. | 0·5 | 0 | 0·5 |
| $4CaO.Al_2O_3.Fe_2O_3$ | 18·2 | 0 | 18·2 |
| Free CaO .. | 0 | 0 | 0·6 |
| $5CaO.3Al_2O_3$ .. | 0 | 0 | 0 |
| Glass .. .. | 0 | 25·5 | 0 |

composed of lime, alumina, silica and ferric oxide are given. The values shown are those obtained (1) when the cement crystallises completely to yield its equilibrium products ; (2) when the cement is cooled so rapidly from a clinkering temperature of 1,450° C.

that the liquid present at this temperature fails to crystallise at
and forms a glass ; (3) when the cement is cooled from 1.4
and the liquid crystallises independently of the
exis⁻⁻⁻⁻

    quilibrium is probably not maintained during      with
the result that the relative proportions of the different cc    unds
present may differ from those calculated on the basis of     e
equilibrium, and part of the liquid may fail to crystallis
glass.   The extent of the glass formation cannot be es
it is probable that the liquid does partially crystallise.

    In stabilised dolomite clinker, the amount of :
during burning will be considerably less than that
portland cement, due to the lower content of the
compounds such as calcium aluminates, $4CaO.Al_2O$    and
$2CaO.Fe_2O_3$.   Hence the difference between the const    cal-
culated on the basis of complete equilibrium will not be    to
deviate much from the actual constitution.

    In manufacturing dolomite bricks from the clinker, the
bricks are fired slowly and then slowly cooled, so that
further time for crystallisation of any glass occurring in the
The constitution calculated on the basis of complete equ
should then apply more accurately to the bricks than the
The experimental clinkers of this investigation were coole

TABLE XXI.—DATA ON CONSTITUTION OF DOLOMITE PRODUCTS.

| Material. | | 2. | |
|---|---|---|---|
| Chemical analysis (per cent.) :— | | | |
| CaO | 23·12 | 18·37 | 37·80 |
| $SiO_2$ | 7·60 | 6·08 | 15·92 |
| $Al_2O_3$ | 0·04 | 1·49 | 1·02 |
| $Fe_2O_3$ | 5·76 | 6·87 | 3·62 |
| g | 63·48 | 67·19 | 40·68 |
| Calculated constitution (per cent.) :— | | | |
| Periclase, MgO .. | 63·48 | 67·19 | 40·68 |
| Free lime, CaO .. | — | — | — |
| $3CaO.SiO_2$ | 19·76 | 2·36 | 18·0 |
| $2CaO.SiO_2$ | 6·88 | 15·65 | 32·1 |
| $4CaO.Al_2O_3.Fe_2O_3$ | 0·19 | 7·10 | 4·90 |
| $2CaO.Fe_2O_3$ | 9·69 | 7·70 | 3·40 |
| $3CaO.Al_2O_3$ | | | |
| Constitution indicated by X-ray photographs :— | | | |
| Free lime, CaO .. | | | |
| $3CaO.SiO_2$ | Present | | Present |
| $2CaO.SiO_2$ | | Present $\beta$ | Present $\beta$ |
| $4CaO.Al_2O_3.Fe_2O_3$–$2CaO.Fe_2O_3$ solid solution | Present | Present | |
| Periclase, MgO | Present | Present | Present |
| $3CaO.Al_2O_3$ | | | |

turnace from 1,550° to 1,000° C. in about 30 minutes. The fact that equilibrium calculations apply is an indication that there is little glass formation in the clinkers.

Further conclusive evidence that the calculations apply to commercially prepared stabilised dolomite clinkers and bricks was obtained by examination of a variety of such materials. The



Fig. 26.—Powder X-ray photographs of three commercial dolomite products.

chemical analyses and calculated constitutions of a selection of the materials tested are given in Table XXI. The X-ray photographs of these products are shown in Fig. 26. The constitutions as indicated by X-rays are also given in Table XXI.

Materials (1) and (2) have low lime contents, approximately 20 per cent., hence the percentage of lime compounds is low, approaching the visibility limit of the X-ray method. Nevertheless, although the patterns of the lime compounds are faint, it has been possible to identify them.

CONCLUSIONS.

Although the patent literature abounds with methods of stabilising dolomite, and many technical publications on this subject have appeared, there are, in the literature, very few systematic studies of the mechanism of stabilisation and the constitution of the clinker. The results of this investigation confirm the previous studies [1,2] which enable the constitution of stabilised clinkers to be calculated from their analyses. The properties of the stabilised dolomite clinkers can now be considered as a function of their compound content. In a later publication it is intended to correlate the behaviour of the clinker and the bricks with the constitution.

Examination of the results of the dolomite $B-Fe_2O_3$ series, reveals that ferric oxide combines with lime to form dicalcium ferrite.

This is of interest in connection with the durability of rammed hearths of calcined dolomite in basic steel furnaces. Iron oxide formed by oxidation of the charge attacks the lime, forming initially $2CaO.Fe_2O_3$, thus fluxing the hearth. The progress of the reaction after the free lime is combined cannot be stated from the results of this investigation, but further work along these lines might elucidate the problem.

### REFERENCES.

1. J. R. Rait and A. T. Green. This Report, p. 13.
2. J. R. Rait and H. J. Goldschmidt, *Bull. B.R R.A.* **56**, 242, 1940. This Report, p. 49.
3. R. B. Sosman and H. E. Merwin, *J. Wash. Acad. Sci.*, **6**, 532, 1916.
4. J. White, R. Graham and R. Hay, *J. Iron and Steel Inst.*, **131**, 91, 1935.
5. G. A. Rankin and F. E. Wright, *Amer. J. Sci.*, **39**, 1, 1915.
6. F. M. Lea and T. W. Parker, *Phil. Trans. Roy. Soc.*, **234**, 1, 1934.
7. F. A. Steele and W. P. Davey, *J. Amer. Chem. Soc.*, **51**, 2283, 1939 ; *Z. Krist*, **73**, 17, 1930.
8. W. C. Hansen, L. T. Brownmiller and R. H. Bogue, *J. Amer. Chem. Soc.*, **50**, 396, 1928.
9. R. Glocker, "Materialprüfung mit Röntgenstrahlen," Julius Springer, Berlin, 1936.
10. H. F. McMurdie and H. Insley, *Bureau Standards J. Research*, **16**, 467, 1936.
11. F. P. Hall and H. Insley, *J. Amer. Ceram. Soc.*, **16**, 459, 1933 ; **21**, 113, 1938.
12. I. Weyer, *Zement*, **20**, 96, 1931.
13. O. Anderson and H. C. Lee, *J. Wash. Acad. Sci.*, **23**, 338, 1933.
14. F. M. Lea and C. H. Desch, " The Chemistry of Cement and Concrete," Edward Arnold and Co., London, 1935.
15. L. T. Brownmiller and R. H. Bogue, *Amer. J. Sci.*, **20**, 241, 1930.

# A Study of the Reactions between Dolomite and Various Minerals (Cont.).

## Part IV.—X-Ray Examination of the Sinters containing Zirconia.*

By J. R. Rait, B.Sc., A.R.T.C., Ph.D., and
H. J. Goldschmidt, M.Sc.

Abstract.

Specimens of fired mixtures of dolomite with various proportions of zirconia, synthetic zircon, natural zircon, and baddeleyite have been submitted to X-ray analysis by the Debye-Scherrer powder method. From the photographs obtained, conclusions regarding the constitutions of the sinters have been made which substantiate those made previously on the basis of determinations of uncombined lime, steam hydration indices and from a consideration of the available thermal equilibrium data. It is confirmed that calcium metazirconate is formed by reaction of zirconia or zircon with the lime. Magnesia remains uncombined as periclase.

Introduction.

The materials which have formed the subject of the experiments described in this paper are fired mixes of dolomite with various proportions of zirconium minerals. These were placed in Group 3 in the classification adopted in Part I.[1] The X-ray examination of the Group I series of clinkers has already been completed and described in Parts II[2] and III.[3] It was found that the constitutions assigned from a consideration of the free lime contents, the steam hydration indices, the available appropriate thermal equilibrium diagrams, and the X-ray diffraction data were in complete accord.

Experimental.

*Materials.*

Analyses of materials used in preparing the dolomite clinkers ·examined are given in Table XXII.

Table XXII.—Percentage Analyses of Raw Materials.

| | $SiO_2$. | $Al_2O_3$. | $Fe_2O_3$. | $TiO_2$. | $ZrO_2$. | $CaO$. | $MgO$. | Loss on Ignition. |
|---|---|---|---|---|---|---|---|---|
| Dolomite B | 3·86 | 0·99 | 0·98 | 0·12 | — | 29·27 | 20·00 | 44·45· |
| Baddeleyite | 6·08 | 2·92 | 7·24 | 2·06 | 76·24 | — | — | 2·56 |
| Zircon .. | 32·58 | 1·29 | 0·67 | 6·72 | 57·26 | — | — | 0·14 |

The zirconia and synthetic zircon which were also used were regarded as pure.

*Procedure.*

The technique was the same as that described previously.[2,3]

*Preparation of the Standards.*

The preparation of $3CaO.SiO_2$, $\beta$- and $\gamma$- $2CaO.SiO_2$, $4CaO.Al_2O_3$. $Fe_2O_3$,· $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, $CaO$, and $MgO$ have been previously described.[2,3]

$CaO.ZrO_2$. Pure calcium carbonate and zirconia were thoroughly mixed in the correct proportions, bonded with collodion, and fired in a special carbon tube resistance furnace to a temperature of over 2,000° C. The material was crushed, bonded, and refired until a homogeneous product was obtained. To prevent carbide formation, air was drawn through the tube to maintain slightly oxidising conditions, and the specimens were placed on a sheet of molybdenum.

J. W. Mellor [4] has summarised the available information on
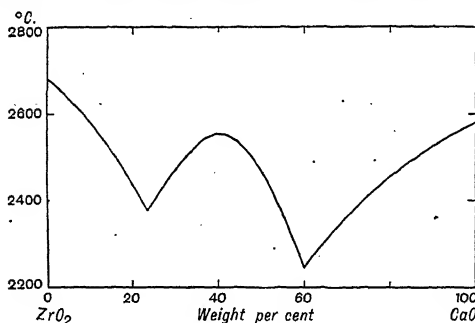


Fig. 27.—Binary system CaO–ZrO$_2$ (after H. Wartenberg and W. Gurr).

calcium zirconate. L. Ouvrard [5] obtained calcium metazirconate (CaO.ZrO$_2$) by heating a mixture of zirconia and fused calcium chloride for 20–30 hours. After leaching with water, a crystalline mass remained. F. P. Venable and T. Clarke [6] obtained the same compound by heating a mixture of zirconia and calcium oxide for several hours, and washing the product with dilute acetic acid. The crystals obtained by L. Ouvrard had a marked action on polarised light. J. W. Mellor [4] has stated that while soda and potash have a great tendency to form polyzirconates, the alkaline earths give the normal metazirconates. More recently H. Wartenberg and W. Gurr [7] have determined the melting diagram of the binary system CaO–ZrO$_2$. Their diagram, which is reproduced in Fig. 27, shows the existence of only one compound, namely calcium metazirconate (CaO.ZrO$_2$).

The material prepared by the authors was a pink- to buff-coloured crystalline sinter. White's free lime test showed that all the lime was combined, and the X-ray pattern (see Fig. 28) was quite characteristic; the patterns of CaO and $ZrO_2$ were not evident.



Fig. 28—X-ray powder photographs of fired dolomite clinkers containing zirconia.

1. $CaO.ZrO_2$.
2. 80 per cent. Dolomite B—20 per cent. Zirconia.
3. 77 ,, ,, 23 ,, ,,
4. 75 ,, ,, 25 ,, ,,
5. 73 ,, ,, 27 ,, ,,

The X-ray photographs of $CaO.ZrO_2$ and the various series of clinkers are shown in Figs. 28 to 31. The photographs of the other compounds concerned have been given previously.[2,3]

*Experimental Results.*

The results calculated according to the procedure described in Part I [1] are given in Table XXIII, in which the results of X-ray analysis are also included. The method of interpretation of these photographs was the same as that developed in the previous investigations.[2,3]

The crystal structures of the calcium silicates and $CaO.ZrO_2$ are much more complex than those of CaO and MgO; their X-ray patterns are more complicated, consisting of a large number of lines. The pattern of $CaO.ZrO_2$ consists of a number of very strong lines, which makes it readily distinguishable from the other

patterns, even when small percentages of the compound are present in the mixtures. It was also possible to identify the patterns of the silicates, CaO and MgO, even in the presence of large amounts of $CaO.ZrO_2$, for although a number of lines coincided, characteristic lines of each pattern could be found unless



Fig. 29.—X-ray powder photographs of fired dolomite clinkers containing zirconia.

1. 95 per cent. Dolomite B— 5 per cent. Baddeleyite.
2. 90        ,,         ,,        10
3. 85        ,,         ,,        15
4. 83        ,,         ,,        17
5. 80        ,,         ,,        20
6. 77        ..         ,,        23
      75                         25

limit of visibility had been reached. The patterns of $).Al_2O_3.Fe_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and calcium titanate were not found in any of the series, since when these compounds were present their amounts were below their limits of visibility in the X-ray powder method. Comparison of the results of

Table XXIII shows that the calculated and X-ray findings are in complete agreement.   The arrows in Table XXIII indicate increasing amounts of phases which were determined by visual estimation of intensities.   In previous quantitative estimations, photometer measurements were made, but scrutiny of the photographs (Figs. 28 to 31) shows that such measurements are unnecessary in this case. All the data obtained by steam hydration experiments, qualitative and quantitative free lime analyses, phase equilibria calculations, and



Fig. 30.—X-ray powder photographs of fired dolomite clinkers containing zirconia.

| 1. | 97 per cent. Dolomite B— | 3 per cent. Synthetic Zircon. |
| 2. | 95  ,,  ,,  ,, | 5  ,,  ,,  ,, |
| 3. | 93  ,,  ,,  ,, | 7  ,,  ,,  ,, |
| 4. | 88  ,,  ,,  ,, | 12  ,,  ,,  ,, |
| 5. | 85  ,,  ,,  ,, | 15  ,,  ,,  ,, |

X-ray analyses are in complete accord, no case existing where the results of different methods are in conflict.   Further evidence is obtained from the " dusting " of the mixture 83 per cent. dolomite —17 per cent. zircon which by calculation had about 40 per cent. $2CaO.SiO_2$ ; the X-ray photograph shows a large amount of $\gamma$-$2CaO.SiO_2$.   Although some of the compounds ($4CaO.Al_2O_3.$ $Fe_2O_3$, $3CaO.Al_2O_3$, $5CaO.3Al_2O_3$, and $2CaO.TiO_2$) are not detected by X-rays, evidence for their existence is obtained by combining the results obtained by the various methods of investigation.

*Phase Equilibria and Reactions.*

The results recorded in Part I,[1] together with those obtained by the present X-ray analysis, give information regarding the reactions and phase equilibria of that part of the six-component ($CaO–MgO–Al_2O_3–Fe_2O_3–SiO_2–ZrO_2$) system involved. The part of that system relevant to the present study is defined by the compounds $CaO$, $MgO$, $2CaO.SiO_2$, $CaO.ZrO_2$, $5CaO.3Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$. Evidence for the occurrence in appropriate compositions at equilibrium of the intermediate compounds $3CaO.SiO_2$ and $3CaO.Al_2O_3$ has already been given for the simpler
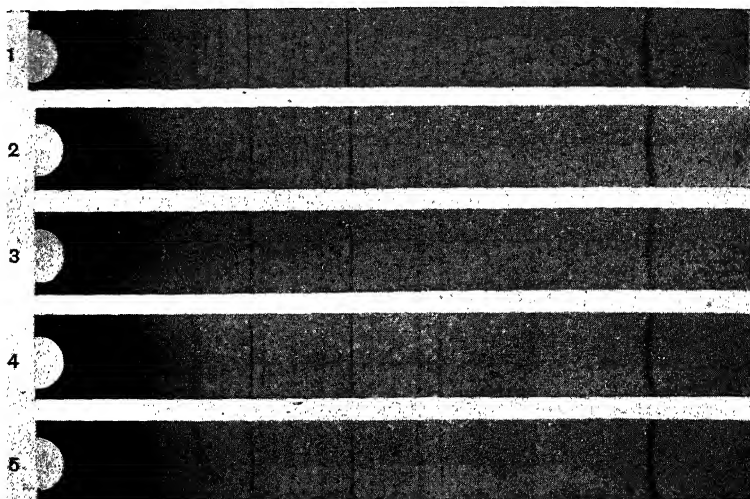


Fig. 31.—X-ray powder photographs of fired dolomite clinkers containing zirconia.

1. 95 per cent. Dolomite B— 5 per cent. Natural Zircon.
2. 90   ,,      ,,    10   ,,      ,,      ,,
3. 88   ,,      ,,    12   ,,  -   ,,      ,,
4. 85   ,,      ,,    15   ,,      ,,      ,,
5. 83   ,,      ,,    17   ,,      ,,      ,,

five-component system in which zirconia is absent.[3] In the presence of zirconia, the same compounds have been found.

The X-ray evidence has substantiated the deduction made in Part I[1] that calcium metazirconate ($CaO.ZrO_2$) is the only compound formed between lime and zirconia, and further that zircon, $ZrO_2.SiO_2$, the only zirconium silicate, is unstable in the presence of lime being decomposed according to either of the following equations :

$$4CaO + ZrO_2.SiO_2 \rightarrow 3CaO.SiO_2 + CaO.ZrO_2$$
$$3CaO + ZrO_2.SiO_2 \rightarrow 2CaO.SiO_2 + CaO.ZrO_2$$
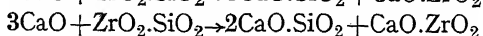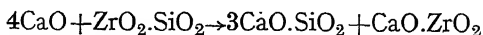
| Dolomite B, per cent. | Stabiliser, per cent. | Mineralogical Constitution as determined by X-rays. | | | | | | Calculated Mineralogical Composition, Weight per cent. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Free CaO. | Periclase ($MgO$). | $3CaO.SiO_2$. | $2CaO.SiO_2$. | $CaO.ZrO_2$. | $2CaO.TiO_2$. | Periclase ($MgO$). | Free CaO. | $3CaO.SiO_2$. | $4CaO.Al_2O_3.Fe_2O_3$. | $3CaO.Al_2O_3$. | $2CaO.SiO_2$. | $5CaO.3Al_2O_3$. | $CaO.ZrO_2$. | $2CaO.TiO_2$. |
| | **Zirconia.** | | | | | | | | | | | | | | | |
| 80 | 20 | P ← | P | tr ← | | P | | 24.8 | 6.4 | 18.2 | 3.7 | 1.2 | | | 45.1 | |
| 77 | 23 | P | P | tr | | P | | 23.4 | 3.3 | 17.2 | 3.5 | 1.1 | | | 50.9 | |
| 75 | 25 | tr | P | tr | | P | | 22.5 | 1.4 | 16.5 | 3.3 | 1.1 | | | 54.6 | |
| 73 | 27 | | P | tr | | P → | | 21.6 | | 14.1 | 3.2 | 1.0 | 1.3 | | 58.2 | |
| | **Synthetic zircon.** | | | | | | | | | | | | | | | |
| 97 | 3 | P | P | P → | | tr → | | 32.9 | 16.5 | 34.9 | 4.9 | 1.6 | | | 8.5 | |
| 95 | 5 | P | P | P → | | P | | 31.7 | 11.5 | 38.2 | 4.7 | 1.5 | | | 11.7 | |
| 93 | 7 | P | P | P max. | | P | | 30.0 | 4.3 | 42.8 | 4.5 | 1.5 | | | 16.3 | |
| 88 | 12 | | P | P ← | | P | | 28.9 | | 44.5 | 4.3 | 1.4 | 1.0 | | 19.3 | |
| 85 | 15 | | P | | P (β) | P → | | 27.3 | | 21.4 | 4.1 | 1.3 | 21.7 | | 23.6 | |
| | **Natural zircon.** | | | | | | | | | | | | | | | |
| 95 | 5 | P ← | P | P → | | P | | 32.9 | 15.6 | 34.9 | 5.1 | 1.8 | | | 7.2 | 1.9 |
| 90 | 10 | tr | P | P max | | P | | 30.0 | 3.0 | 42.6 | 4.8 | 1.8 | | | 13.9 | 3.1 |
| 88 | 12 | | P | P ← | tr (β) | P | | 28.9 | | 38.0 | 4.7 | 1.9 | 5.8 | | 16.4 | 3.6 |
| 85 | 15 | | P | tr | P γ | P | | 27.3 | | 14.0 | 4.6 | 1.9 | 27.1 | 1.1 | 20.1 | 4.3 |
| 83 | 17 | | P | | (tr β) | P → | | 26.3 | | | 4.5 | 0.3 | 39.8 | | 22.5 | 4.7 |
| | **Baddeleyite.** | | | | | | | | | | | | | | | |
| 95 | 5 | P ← | P | P → | | P | | 32.8 | 21.9 | 26.1 | 6.8 | 1.2 | | | 9.6 | 0.5 |
| 90 | 10 | P | P | P | | P | | 30.2 | 14.2 | 26.0 | 8.2 | 0.7 | | | 18.6 | 1.3 |
| 85 | 15 | P | P | P | | P | | 27.5 | 7.6 | 25.8 | 9.4 | 0.2 | | | 26.9 | 1.6 |
| 83 | 17 | | P | P | | P | | 26.5 | 4.6 | 25.8 | 9.9 | 0.2 | | | 30.2 | 1.7 |
| 80 | 20 | | P | P | | P | | 25.0 | 1.0 | 25.6 | 10.2 | | | | 34.8 | 1.9 |
| 77 | 23 | | P | tr ← | | P | | 23.6 | | 14.6 | 10.4 | | 8.3 | | 39.2 | 2.0 |
| 75 | 25 | | P | | tr (β) | P → | | 22.7 | | 5.0 | 10.7 | | 15.4 | | 42.1 | 2.1 |

P indicates the presence of the compound.
tr indicates the presence of a trace of the compound.
P max indicates the presence of the maximum amount of the compound in the series.

It would appear from the work of H. Wartenberg and H. Wert [8] that there is only one compound of magnesia with zirconia, although this is contested by N. A. Shirnova.[9] However, as in the case of the magnesium silicates, the evidence of the X-ray analysis and that already given in Part I [1] indicates that the reaction :

$$CaO + MgO.ZrO_2 \rightarrow CaO.ZrO_2 + MgO$$
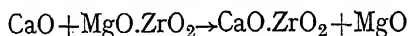
occurs at high temperatures, the calcium metazirconate and periclase persisting at room temperature.

Since the lattice spacing of each compound present remained constant, it can be assumed that any solid solution in the six-component system is small.

## Technical Applications.

In the production of stabilised dolomite clinker for the manufacture of dolomite bricks, the lime must be completely combined to form a refractory compound with a low hydration index. The binary diagram $CaO-ZrO_2$ [7] (see fig. 27) indicates that $CaO.ZrO_2$ is a very refractory compound (M.P. 2,500° C.) and that the lowest melting-point is about 2,200° C. According to J. W. Mellor [4] there are extensive deposits of baddeleyite (over 70 per cent. $ZrO_2$) in Brazil; prior to the discovery of baddeleyite, zircon was the most important source of zirconium.

The analyses of the ores used in the present investigations, and given in Table XXII, are typical of these deposits.

The minimum amounts of baddeleyite and zircon required to stabilise dolomite B were 22 per cent. and 11 per cent. by weight respectively. The corresponding steam hydration indices were 3·8 per cent. and 3·0 per cent., which compare favourably with the hydration indices of clinkers stabilised by the minerals studied in Group 1.[1]

The clinkers containing zirconia are very refractory and have sufficiently low hydration indices to allow the satisfactory pressing of bricks from the clinker moistened with water. The properties of such bricks have yet to be investigated.

## REFERENCES.

1. J. R. Rait and A. T. Green.   This Report, p. 13.
2. J. R. Rait and H. J. Goldschmidt.   *Ibid.*, p. 49.
3. J. R. Rait and H. J. Goldschmidt.   *Ibid.*, p. 63.
4. J. W. Mellor, " A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. VII, Longmans, Green & Co., Ltd., London, 1927.
5. L. Ouvrard, *Compt. Rend.*, **112,** 1,444, 1891 ; **113,** 80, 1891.
6. F. P. Venable and T. Clarke, *J. Amer. Chem. Soc.*, **18,** 434, 1896.
7. H. Wartenberg and W. Gurr, *Z. anorg. allgem. Chem.*, **196,** 374, 1931
8. H. Wartenberg and H. Wert, *ibid.*, **190,** 179, 1930.
9. M. A. Shirnova, *J. Prikl. Chim.*, **12,** 1,286, 1939.

# (3) A Note on a Simple Partially Stabilised Dolomite Mixture.*

By W. J. REES, D.Sc.(Tech.), F.I.C.

Some years ago the author, in investigating the stabilising of dolomite, examined the effect of the addition of comparatively small proportions of clay and iron oxide. One of these mixtures, viz. ground dolomite, 95 per cent. ; ball clay, 2·5 per cent. ; mill scale, 2·5 per cent., by weight, gave a promising result and behaved exceptionally well when used as a crushed aggregate for a basic hearth. Its "keeping" property was much superior to that of ordinary dead-burnt dolomite and its sintering characteristics in the hearth were particularly good. A mixture of this type could be dead-burned satisfactorily on a commercial scale in a rotary kiln.

Some further experiments have been made recently with the above mixture, as follows. A quantity of the mixture was tempered with 10 per cent. water containing a little sulphite lye. This was made into briquettes which after drying were burned at 1,500° C. The burnt briquettes showed a shrinkage of approximately 30 per cent., were brown-black in colour, and strong. Some of the briquettes were left exposed to the atmosphere in the laboratory for 6 weeks, and whilst they had greyed over on the surface they were still strong and showed no disintegration.

A number of the burnt briquettes were crushed and made into test-pieces measuring $2\frac{1}{2}$ in. $\times$ 2 in. $\times$ 2 in. to the following gradings, using linseed oil for tempering and to give green and dry strength :

|  | A | B |
|---|---|---|
| −7+25 B.S.S. : | 45 per cent. by weight ; | 65 per cent. by weight. |
| −25+72 B.S.S. : | 10 ,, ,, | — ,, ,, |
| −72 B.S.S. : | 45 ,, ,, | 35 ,, ,, |

After drying, these test-pieces were fired in the laboratory gas-fired furnace at 1,520°–1,550° C.

The firing shrinkage was A : 1·8 per cent. and B : 4·2 per cent. ; a hydration test (100 mesh material in steam for 5 hours) gave an increase in weight of 14·8 per cent.

Refractoriness-under-load tests (28·5 lb. per sq. in. load) gave the following results :

|  | A | B |
|---|---|---|
| Expansion ceased at .. | 1,420° C. | 1,470° C. |
| Deformation began at .. | 1,460° C. | 1,540° C. |
| 10 per cent. squatting at | 1,540° C. | 1,570° C. |

The spalling resistance determined by the usual method at 900° C. (15-minute cycles) gave A, 3 to 5 reversals, and B, 4 to 5 reversals.

The resistance to corrosion by a basic open-hearth slag at 1,600° C. for 4 hours was examined; there was slag absorption, but very little corrosion in either the A or B test-pieces.

A chemical analysis of the fired briquettes gave : CaO, 52·05 ; MgO, 34·82 ; $Fe_2O_3$, 5·08 ; $Al_2O_3$, 3·41 ; $SiO_2$, 4·30 ; and loss-on-ignition, 0·40 per cent.

The results obtained in the above trial mixture seem to be sufficiently promising to warrant a trial on a larger scale than is possible in the laboratory ; especially as, judging by the laboratory tests, bricks made from it appear likely to have a better slag resistance and spalling resistance than bricks made from a dolomite which has been completely stabilised by the addition of silica, or a silicate such as serpentine, etc., sufficient to convert the lime into the di- or tricalcium silicate.

It is not suggested that bricks made from the mixture used (with a firing temperature near to that used in the laboratory) would be so stable to ordinary atmospheric conditions as the completely stabilised bricks, but the indications are that they would certainly keep for some weeks without any change through hydration.

# Section C.   Blast-Furnace Refractories.

## (4) The Influence of Working Conditions on the Durability of Blast-Furnace Linings.*

By G. R. RIGBY, Ph.D., B.Sc., A.R.C.S., D.I.C., A.I.C., and
A. T. GREEN, F.I.C.

ABSTRACT.

The conditions prevailing during a blast-furnace campaign are first analysed. Collected data indicate the wide variations which have occurred in the stacks of different blast furnaces due to segregation of the burden. Factors governing burden distribution are shown to have an important influence on the temperatures prevailing at the lining face. Abnormal conditions in the stack are considered to cause channelling of the lining in specific parts of the furnace. The reported investigations on the linings of blown-out furnaces are reviewed and data obtained from a number of recently blown-out furnaces are also incorporated. A summary is given of the laboratory investigations on such important aspects of refractory materials as carbon monoxide disintegration, alkali attack, and the action of blast-furnace slags.

The properties which refractory materials for blast furnaces should possess are considered in the section dealing with the choice of materials for the lining. The final sections of the paper are devoted to a discussion of the influence of water cooling in the stack, the effect of insulation, and the blowing-in of the furnace.

INTRODUCTION.

During the last decade investigations on the durability of blast-furnace linings have followed two well-defined methods of approach. First, examinations of blown-out furnace linings have been undertaken, the blowing-out lines have been carefully measured, and samples of the linings have received detailed investigation in the laboratory. By this means the various factors militating against the life of the lining have been assessed, and this in turn has suggested the long-range laboratory investigations which have formed the second method of approach. Among these laboratory investigations may be cited the resistance of refractory materials to carbon monoxide, alkalies, and slag attack, problems of particular moment where blast-furnace refractories are concerned. Researches on the more general properties of refractory materials have also received attention. These include the investigations on the refractoriness-under-load test and on the properties of jointing cements which have recently been carried out at the Mellor Laboratories.

However, the general problem is still fraught with difficulties, mainly because the linings of blast furnaces, unlike those of steel

* *Bull. B.R.R.A.*, 55, 39, 1940.

furnaces, for example, cannot be examined periodically during the furnace campaign. There has long been a suspicion that excessive wearing back of the lining in the bosh and at positions in the lower stack occurs comparatively early in the life of the. furnace. Until recently experimental verification of this point was lacking. However, an investigation has now been instigated which bids fair to permit the rate at which the lining wears to be assessed.· In brief, this consists of inserting a number of thermocouples in various planes of a furnace at definite distances behind the working face, and taking temperature records throughout the entire furnace campaign. This investigation, although commenced only recently, has already yielded results of great interest, and has been further extended to contrast the conditions of linings in furnaces with and without water-cooled stacks.

I. The Conditions Prevailing in the Furnace.

(a) *Conditions in the Stack.*

In selecting refractory materials for service it is essential to appreciate the conditions which they are required to withstand. Perhaps the most fundamental one is that of temperature, but continuous measurements of the temperature gradients through blast-furnace linings are lacking. Temperatures at the inwall of the stack have, however, been reported, mainly in connection with researches on blast-furnace gas reactions. A representative series of these stack temperatures, together with the carbon dioxide and carbon monoxide contents of the furnace gases, are set out in Table XXIV. In order to assist in comparing data, the distances below the stock line at which observations were taken, are approximated to the nearest foot. The figures given for furnace C are computed from the authors' investigations on temperature gradients through blast-furnace linings.

Perhaps the most striking feature of Table XXIV is that for furnaces making the same type of iron and with similar outputs, the inwall temperatures, particularly in the upper regions of the stack, can differ over wide limits. For example, furnace C had an inwall temperature of 905° C. at a position 5 ft. below the stock line, whereas furnace A at a position 10 ft. below the stock line had an inwall temperature of only 390° C. The stack temperatures of furnace A increased towards the centre of the burden, where they became comparable with the inwall temperatures of furnace C. The American furnace F had inwall temperatures corresponding to those of furnace C, but unlike furnace A the temperatures decreased towards the centre of the burden. The report on furnace A stated that the stock was more porous at the centre of the column, where the temperature and gas velocity were high, and that the change was progressive to the inwall, where the stock was composed of smaller

particles and the gas velocity was low. S. P. Kinney,[4] who is responsible for the data on furnaces D and E, also stated that a high velocity of gas indicated the passage of a large volume of gas through a relatively porous portion of the stock column, and high velocities were in turn indicative of high temperatures.

Another factor of importance in view of the disintegration of linings by carbon monoxide is the CO and $CO_2$ contents of the stack gases which are also recorded in Table XXIV. The positions, says S. P. Kinney,[4] where the gas was high in carbon monoxide content corresponded to the sections of the column where the gas velocity was high, and in turn, to the portion of the shaft where high temperatures existed. In other words, high temperatures, high gas velocities, and optimum carbon monoxide contents in the gas existed together in the furnace stack and these conditions, which obtained at the centre of the stock column in furnace A, were probably present at the lining face in furnaces E, F, and C.

The conditions which obtained in furnace A are favourable to the life of the lining, and after eighteen months, when this furnace was taken off blast owing to trade conditions, the stack lining was inspected and reported to be in sufficiently good condition to allow the furnace to be blown in again on the same lining without need of repair. The reverse conditions which obtained in furnaces C, E, and F are more severe on the lining. A high temperature at the lining face facilitates slag attack, alkali, zinc and lead penetration, and the high gas velocity makes for increased erosion and abrasion, and probably favours the passage of the blast-furnace gas with a high CO content through the brickwork. Referring to furnace E, S. P. Kinney stated that the gas passing through the peripheral layers was practically short-circuiting the charge and he suggested that this was the cause of excessive wear of the lining, particularly around the stock line. Furnace B had relatively porous zones in the stock column both at the centre and periphery, where the highest temperatures were recorded. In this furnace the stack lining was cooled by the insertion of cigar coolers. During the whole campaign this proved a very satisfactory furnace ; it worked smoothly and gave 974,000 tons of basic iron.

The distribution of the gas appears to be of prime importance when considering the life of the lining, but it is a more difficult matter to discover the factors which determine this distribution. Kinney [4] suggested that to decrease the short-circuiting of the gas in furnace E, the bosh and hearth diameters should be decreased and the throat diameter increased, thus giving less batter to the stack. He also recommended a throat of the Venturi type. On the other hand, furnace A had more batter on the stack than furnace C, the stack of the latter being almost cylindrical. It is obvious that the segregation of the burden is a determining factor. As pointed out by A. T. Green and W. Hugill [6] the burden distribution largely depends on (1) the relative diameters of throat and large bell ;

TABLE XXIV.—DATA ON CONDITIONS OF TEMPERATURE AND COMPOSITION OF GASES IN BLAST FURNACES.

| Description of Furnace. | British Blast Furnaces. | | | American Blast Furnaces. | | |
|---|---|---|---|---|---|---|
| | Furnace A (Basic).[1] | Furnace B (Basic).[2] | Furnace C (Basic). | Furnace D (Foundry).[3] | Furnace E (Basic)[4] | Furnace F.[5] |
| No. of tuyeres .. | 8 | 10 hearth, 5 bosh. | 8 | 12 | — | 12 |
| Diameter of hearth<br>Diameter of bosh<br>Diameter of throat<br>Diameter of bell | ft. in.<br>11  6<br>22  0<br>15  0<br>11  0 | ft. in.<br>14  6<br>21  0<br>17  0<br>13  0 | ft. in.<br>10  6<br>16  0½<br>14  3<br>8  6 | ft. in.<br>14  6<br>19  6¼<br>14  0 3/16<br>10  3 | ft.<br>28<br>30<br>19<br>14 | ft.<br>19<br>—<br>17<br>13 |
| Blast pressure, lb./ sq. in . | 7–8 | 8½–9½ | 10–12 | 16 | — | — |
| Weekly output .. | 1,200–1,350 tons. | 1,600 tons approx. | 1,200 tons. | 2,000 tons. | 3,100 tons. | — |
| Temperatures in furnace.<br>3 ft. below stock line. | 270° C. inwall.<br>420° C. 4 ft. in burden. | — | — | 204° C. inwall. | 595° C. inwall.<br>410° C. centre burden. | — |
| 5 ft. below stock line. | — | — | 905° C. inwall. | — | — | — |
| 7 ft. below stock line. | — | — | — | — | — | 755°–1,030°C. inwall.<br>360°–495° C. 4 ft. in burden. |

| | | | | | |
|---|---|---|---|---|---|
| 10 ft. below stock line. | 390° C. inwall. 520° C. 4 ft. in burden. 620° C. 9 ft. in burden. | — | — | 465° C. inwall. | — |
| 16 ft. below stock line. | 480° C. inwall. 620° C. 4 ft. in burden. 750° C. 9 ft. in burden. | — | — | — | 985° C. inwall. 540° C. centre burden. |
| 18 ft. below stock line. | — | 715° C. inwall. 515° C. 4 ft. in burden. 765° C. 10 ft. in burden. | — | — | — |
| 22 ft. below stock line. | — | — | 1,010° C. in-wall. | 740° C. inwall. 765° C. centre. | — |
| 28 ft. below stock line. | 670° C. inwall. 740° C. 4 ft. in burden. 930° C. 9 ft. in burden. | 810° C. inwall. 675° C. 4 ft. in burden. 850° C. 10 ft. in burden. | — | — | — |
| 36 ft. below stock line. | — | 985° C. inwall. 940° C. 4 ft. in burden. 980° C. 10 ft. in burden. | 1,035° C. in-wall. | — | — |
| 44 ft. below stock line. | — | 1,050° C. inwall (scab). 1,060° C. 4 ft. in burden. 1,140° C. 9 ft. in burden. | — | 836° C. inwall. 905° C. centre. | — |

8

TABLE XXIV.—continued.

| Description of Furnace. | British Blast Furnaces. | | | | | American Blast Furnaces. | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | Furnace A (Basic).[1] | | Furnace B (Basic).[2] | | Furnace C (Basic). | Furnace D (Foundry).[3] | | Furnace E (Basic).[4] | | Furnace F.[5] | |
| | $CO_2$%. | $CO$%. | $CO_2$%. | $CO$%. | | $CO_2$%. | $CO$%. | $CO_2$%. | $CO$%. | $CO_2$%. | $CO$%. |
| $CO$ and $CO_2$ contents of gas. | | | | | — | | | | | | |
| 3 ft. below stock line. | 16·3<br>10·9 | 23·6—in-wall.<br>29·8—4 ft. in burden. | — | — | — | 10·6<br>2·9 | 26·5—in-wall.<br>35·2—centre. | 7·0<br>19·0 | 32·0—in-wall.<br>22·3—centre. | — | — |
| 7 ft. below stock line. | — | — | — | — | — | — | — | — | — | 9·8<br>18·3 | 30·2—in-wall.<br>20·4—4 ft. in burden. |
| 10 ft. below stock line. | 14·4<br>10·5<br>4·4 | 26·3—in-wall.<br>30·7—4 ft. in burden.<br>37·5—9 ft. in burden. | — | — | — | 15·1<br>14·6 | 22·2—in-wall.<br>24·2–20 in. in burden. | — | — | — | — |
| 16 ft. below stock line. | 13·6<br>8·5<br>1·6 | 27·5—in-wall.<br>32·4—4 ft. in burden.<br>38·9—9 ft. in burden. | ·| — | — | — | — | 5·6<br>8·0 | 34·0—in-wall.<br>23·0—centre. | — | — |

| | | | | |
|---|---|---|---|---|
| 18 ft. below stock line. | — | — | 34·6—in-wall. 28·3—4 ft. in burden. 36·8—10 ft. in burden. 1·2 11·3 0·3 | — |
| 22 ft. below stock line. | — | — | — | 28·0—in-wall. 26·2—20 in. in burden. 35·2—90 in. in burden. 9·0 12·3 0·5 |
| 28 ft. below stock line. | 31·1—in-wall. 35·4—4 ft. in burden. 39·0—9 ft. in burden. 10·8 6·5 1·3 | — | 38·2—in-wall. 35·1—4 ft. in burden. 39·4—10 ft. in burden. 1·4 5·1 0·5 | — |
| 36 ft. below stock line. | — | — | 37·2—in-wall. 36·6—4 ft. in burden. 37·2—10 ft. in burden. 0·8 0·8 0·2 | — |
| 44 ft. below stock line. | — | — | 38·2—in-wall. 38·5—4 ft. in burden. 38·4—10 ft. in burden. 1·0 0·2 0·0 | 34·4—in-wall 0·3 |

(2) the charging and distributing mechanism, and (3) the relative sizes of the raw materials. According to F. Clements [7] the throat of the furnace should be 4 ft. greater in diameter than the bell. If the bell clearance is small there is a tendency for the fines to accumulate at the walls. There is evidence that this protects the lining to some extent, but at the same time, according to some investigators, leads to irregular working. A bell which is proportionately too small will give rise to a porous zone at the periphery of the burden, and promote short-circuiting of the gas up the sides of the furnace. Short-circuiting of the gases in furnace E was possibly due to the large hearth diameter, the gases never penetrating into the centre of the stock column. In the case of furnace C the small bell and inadequate batter on the stack are suggested as causes. However, opinions must remain conjectural until more data are accumulated on a wide variety of furnaces.

So far we have only considered normal conditions in the stack; the temperatures given in Table XXIV were average values over long periods of the furnace campaign. Superimposed on these conditions are the extraordinary effects which are obtained when for any reason the furnace routine is disturbed. H. W. Johnson,[5] after studying the inwall temperatures in a horizontal plane of an American blast-furnace 10 ft. below the stock line, concluded that when this particular furnace was working normally, the inwall temperatures at every position in the plane were of a similar order, in the region of 650°–750° C. There were periods in the operation of the furnace when the temperature distribution over this plane was irregular; at one period, for example, the four couples read 925°, 870°, 745°, and 690° C. This difference, according to Johnson, was due to an unbalanced gas distribution, and coincided with the furnace driving in an irregular manner. At certain periods, therefore, when a furnace is driving irregularly there is a possibility of certain positions of the lining being subjected to temporary conditions more severe than the normal ones. These intermittent periods of high temperature and increased gas flow probably account for the channelling which is often observed down one side of a furnace. Regions of severe slag attack occasionally found at positions relatively high in the stack can probably be ascribed also to periods of abnormal working. Fig. 32 is a photograph of a blown-out lining where channelling occurred for a distance of two-thirds down the height of the stack. The investigations of the authors on furnace C suggested that in this case channelling was taking place down the side of the furnace immediately over the slag notch. In previous campaigns this furnace has tended to show channelling in the same position, suggesting that the intermittent unbalanced gas flow was caused by features inherent in the structure or working of the furnace.

*(b) Conditions in the Bosh.*

It is generally recognised that temperatures higher than 1,000° C. prevail at the lining face in the bosh region. S. P. Kinney [3] and co-workers gave 1,534° C. as the inwall temperature at the tuyere level of a furnace making foundry iron. The authors have obtained measurements of the temperatures at four positions in the bosh at a plane 9 ft. 4 in. above the centre line of the tuyeres. The thermocouples originally terminated 6 in. behind the bosh lining. The recorded temperatures were very erratic and showed daily fluctuations over a temperature range of about 100° C. These variations



Fig. 32.—Channelling in the lower two-thirds of the stack lining of a blast-furnace.

occurred independently with each couple, and were probably due to localised burden slips causing continual alterations in the flow of the gases. There were indications that scars were being continually formed at the inwall, which suddenly fell off, causing a rise in temperature amounting to as much as 600° C. For example, one couple, which gave an average temperature of 500° C. over a considerable period, rose in the course of a few days to 1,177° C. There were indications that a heavy scar in front of the couple suddenly fell away, exposing the end of the couple to the furnace gases. The removal of these scars appeared to coincide with the furnace driving much more freely. It is not unusual to find in plated boshes

cooled by external sprays that all brickwork is eventually replaced by scars. One blown-out furnace examined revealed large temporary scars in the bosh region, behind which were the bosh plates covered by a hard scar $3\frac{1}{2}$ in. thick, no brickwork remaining.

Attack by fluid slag is often a feature of the lining in the bosh region. The corrosive action of the slag is dependent both on its chemical constitution and physical characteristics such as viscosity. According to F. Hartmann and others, slag attack is greatly reduced by efficient water cooling, as this tends to solidify the slag on the working face, thus actually protecting the brickwork. According to several investigators, in the upper part of the bosh where the slag first appears there is excess of lime and viscous limy slags tend to be formed. S. P. Kinney [8] considered that the slag does not take up its total silica content until it reaches the tuyere level, where the silica in the coke ash is released. C. D. Abell [9] stated that as the slag passes down the bosh it changes from a gehlenitic to an akermanitic variety. Work by R. S. McCaffery, [10] T. P. Colclough, [11] and J. R. Rait and R. Hay [12] has shown that with slags containing 20 per cent. of $Al_2O_3$ and 5 per cent. of MgO a minimum viscosity occurs at a basicity of 1·28–1·35. With a slag containing 5 per cent. MgO and a basicity of 1·4 additions of alumina first decrease and then increase the viscosity, the region of minimum viscosity occurring with about 15–18 per cent. of alumina. It is the general opinion that siliceous slags exert a more corrosive effect on the lining than do the more limy slags, although the actual finishing slag, if siliceous, is perhaps more viscous than a limy slag. The question revolves not only on the viscosity of the finishing slag, but on that of the intermediate slags formed higher in the bosh and carrying a higher lime content. According to viscosity measurements, a blast-furnace slag has a minimum viscosity with a slag ratio of 1·3. Such a finishing slag would presumably contain more lime at positions higher in the bosh, and would consequently be more viscous. On the other hand, a finishing slag with a ratio less than 1·3 would be more viscous in the hearth, but attain its minimum viscosity at some point in the bosh, where the higher lime content would give the ratio of 1·3. Such a slag might conceivably be of sufficient fluidity to cause corrosion of the lining at that position.

## II. Examinations of Blown-Out Furnace Linings.

### (a) The Lining in the Throat.

It is usual to protect the throat in the region of the stock line by some form of armouring. This usually consists of steel or cast-iron striking plates arranged in tiers. Steel is to be preferred, since with certain grades of cast iron there is a tendency for the metal to swell under the influence of the furnace gases. On blowing out the furnace, even when these plates are still in position, it is not uncommon to find that the brickwork immediately behind has disintegrated

due to the action of carbon monoxide. In one furnace examined a considerable amount of abrasion had occurred in the brickwork between the metal bars (Fig. 33), probably due to abnormal gas velocities carrying particles of ore and coke dust.
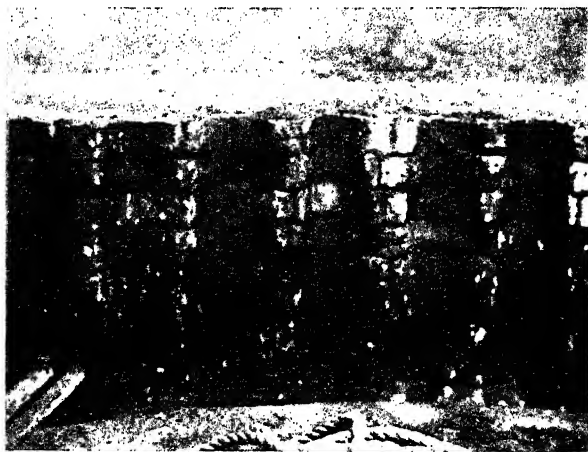


Fig. 33.- -Abrasion of the brickwork between the metal bars in the throat of a blast-furnace lining.

### (b) *The Stack between the Throat and Lintel Plate.*

In the examination of the stack lining some disintegration by carbon monoxide is often the most prevalent feature. High up in the stack the front bricks generally suffer most severely, but lower down the disintegration occurs behind the working face, until at the lintel level the back bricks are affected. It is not uncommon to find in the middle portions of the stack a dense working face, a layer of unattacked brickwork next to the casing, and between the two a powdery disintegrated zone containing much deposited carbon. Laboratory research has demonstrated that disintegration of refractory materials by carbon monoxide is most effective over the temperature range 400°–600° C. and therefore the temperature of the working face, together with the gradients through the lining, determine the zones of maximum potential disintegration in the stack. In one furnace examined the total collapse of a large section of the lining at a position 10 ft. below the throat plates was ascribed mainly to disintegration by carbon monoxide. A sample of brickwork from the stack showing disintegration and carbon deposition is illustrated in Fig. 34.

The presence of zinc salts in the stack lining is a second general feature of blown-out linings. Metallic zinc has a boiling-point of 907° C., but at temperatures as low as 600° C. the vapour pressure is still appreciable, being 11·3 mm. A. T. Green and W. Hugill [6]

considered that zinc as metal, when it filled a void completely, could cause breakdown, since it had a much higher coefficient of thermal expansion than firebrick.    They also concurred in the work of F. Hartmann,[14] who demonstrated in the laboratory that metallic zinc deposited in the pores of a brick and subsequently oxidised caused disruption of the material.    Hartmann found as much as 43 per cent. of zinc in zones of failure of a German blast-furnace, but this appeared to be an exceptional case and B. Osann [15] considered that disruption by zinc rarely occurred unless the metal was oxidised.    The presence of zinc sulphide and zinc oxide in a stack lining has been reported by W. Woodhouse, W. Hugill, and A. T. Green.[13]    They found that brick samples having numerous incipient cracks parallel to the hot face almost invariably revealed, on breaking apart, a layer of zinc sulphide crystals firmly adhering to one face of the fracture and practically none on the opposite face.



Fig. 34.—Brick showing carbon deposition and disintegration.

On the other-hand, W. Feldmann [16] has suggested that the zinc might enter into combination with the brickwork, giving a spinel. He observed a light blue coloration commencing at a depth of 8 in. behind the lining in a position from 3 ft. to 15 ft. above the lintel plate.    These blue-coloured parts were exceedingly hard and Feldmann considered that zinc spinel had been formed.

Beads of metallic lead are often associated with the deposition of zinc salts, and it is not uncommon to find the presence both of zinc sulphide and lead globules at positions where the lining has apparently been disintegrated by carbon monoxide.    Up to the present it is difficult to say what effect the zinc compounds and lead globules have on the durability of the lining.    The present authors have noticed the condensation both of beads of metallic lead and of zinc chloride on thermocouples placed in the stack lining at a distance of 22 ft. below the stock line.

The accumulation of alkali salts has long been considered

a contributory cause of the failure of blast-furnace refractories in the stack region. F. H. Clews and A. T. Green [17] have reported from 19·46 to 21·48 per cent. of alkalies in the zone of a blast furnace, 30 ft. down the stack. They said that the alkalies were volatilised in the hotter portions of the furnace and the gases, charged with small amounts of alkali vapour, could then attack the refractories throughout the length of the stack. Prussic acid is also synthesised in small amounts in the furnace so that the formation of alkali cyanides can occur, with subsequent deposition in the cooler portions of the brickwork around the casing and in particular in brickwork surrounding stack coolers. The alkali is thus free to combine with the lining either in the gaseous, liquid, or solid condition. C. L. Beattie and others [18] have reported the presence of sodium and potassium carbonates and caustic potash in blown-out linings. F. H. Clews and A. T. Green [17] on analysing the slag adhering to the working face of the brickwork at a position 25–33 ft. down the stack, found the following composition : $SiO_2$, 63·24 per cent. ; $Al_2O_3$, 24·11 per cent. ; FeO, 4·55 per cent. ; MnO, 0·32 per cent. ; CaO, 0·35 per cent. ; MgO, 1·11 per cent. ; $Na_2O$, 1·01 per cent. ; $K_2O$, 3·86 per cent. ; $TiO_2$, 0·50 per cent. ; carbonaceous matter, 0·97 per cent. At the same region in the stack, but within the lining, was a second slag of up to $1\frac{1}{2}$ sq. in. cross-section extending across the whole section, of analysis : $SiO_2$, 66·31 per cent.; $Al_2O_3$, 15·83 per cent. ; $Na_2O$, 2·66 per cent. and $K_2O$ 10·59, per cent. The same authors reported a jelly-like material found at a position where falling in of a lining had occurred. This consisted of a little cyanide and a considerable quantity of alkali silicate.

It is obvious that alkali vapours are not only deposited as salts, *e.g.* cyanides and carbonates, in the brickwork but actually attack the lining, corroding the brickwork and in certain instances may cause collapse of a portion of the lining. The present authors found considerable deposits of ammonium chloride at the cold end of steel tubes which penetrated a furnace lining to depths of 2 ft. 9 in. behind the face at various positions in the stack. This suggests that the gases in the stack contain traces of hydrochloric acid gas or chlorine, which may assist the volatilisation into the brickwork of zinc, alkalies, and iron as chlorides.

In addition to definite inclusions found in the lining, there is ample evidence of the stack brickwork suffering both by spalling and slagging. On examining samples of a lining under the micro-scope, A. T. Green, W. Hugill, and H. Ellerton [19] detected that the quartz in the brickwork had been transferred to cristobalite, indicating that temperatures of over 1,000° C. had existed within 15 ft. of the top of the furnace. Slag attack was distinctly evident 30 ft. down the stack and gehlenite crystals were detected in a glassy matrix on the refractory surface. One of the chief effects of this slag attack was the weakening of the material at a position behind the glassy slag layer resulting in the spalling of the brickwork.

At the lower zones of the stack, slag attack is generally more pronounced.

The blowing-out lines of blast-furnaces which have become available generally showed some wearing back of the lining throughout the whole stack. The chief position of wear, however, appeared to be a zone at the bottom of the stack about 10–16 ft. above the lintel plate. The tendency for the lining to fail in this position might possibly be retarded by continuing the bosh water cooling into the lower stack region. The blowing-out lines of a typical furnace are illustrated in Fig. 35. The formation of scars, prevalent in the bosh, was not usually met with except in the lower stack. An exception occurred, however, with furnace B (Table XXIV). This furnace had worked very satisfactorily for 12 years and had produced 974,000 tons of basic iron. After blowing out it was found that a large scar had formed between the second and sixth row of cigar coolers, 19 ft. and 35 ft. below the stock line. There was every reason to believe that this scar had formed during the last two years of the furnace campaign. Commencing from the casing it consisted of (1) 9 in. of unaltered brick, (2) 1 ft. 3 in. of loose material comprising disintegrated brick impregnated with much carbon and beads of lead, and (3) 2 ft. 6 in. of hard scar, a white, rock-like material which at the face was laminated and could be peeled off in successive layers. These layers consisted of alternate deposits of burden and metallic iron, which was almost free from carbon and was consequently very tough and pliable. One suggestion for this scar formation was that certain of the coolers in the vicinity had been leaking, while a second suggestion attributed the scar formation to intermittent working of bosh tuyeres. Both these theories have definitely been shown by the management to be untenable and at the present it is not known with certainty to what this scar formation is due. The scar, however, in no way interferred with the normal driving of this furnace, which was finally blown out owing to trade conditions. The blowing-out lines are shown in Fig. 36.

(c) *The Bosh Lining.*

W. Woodhouse, W. Hugill, and A. T. Green [13], after a careful examination of the bosh linings of three furnaces, found that the front brickwork showed signs of intense erosion and slag attack. They also considered that slag attack towards the lower zones of the bosh would have been much more violent except for the water cooling employed. The brickwork behind the working face gave evidence of disintegration due to carbon deposition. Zinc salts, particularly the sulphide, were also found associated with the brickwork behind the highly vitrified face.

The present authors, by inserting thermocouples in a bosh lining, found that rapid erosion occurred during the early stages of a furnace campaign. At a position 9 ft. 4 in. above the tuyeres it

Fig. 35.—Sections through a typical furnace showing original furnace lines and lines after blowing out: section 1, 2 on the left; section 3, 4 on the right.

———————— Original brickwork.
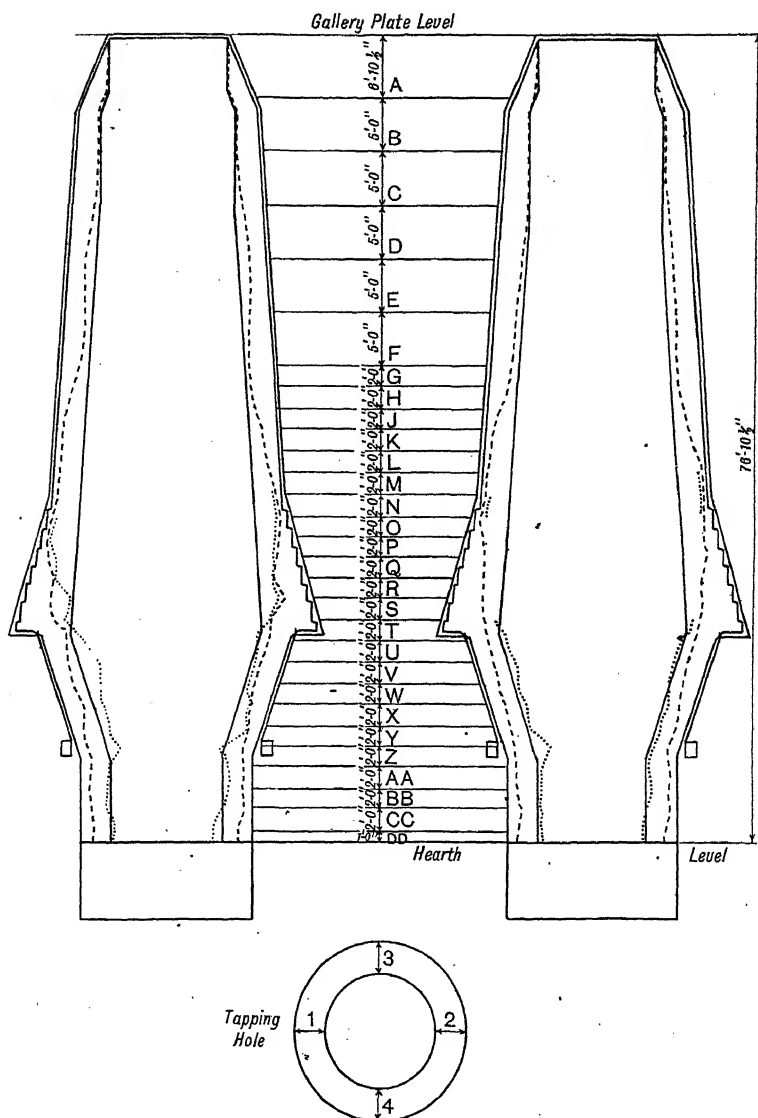· · · · · · · · · · · · Scar.
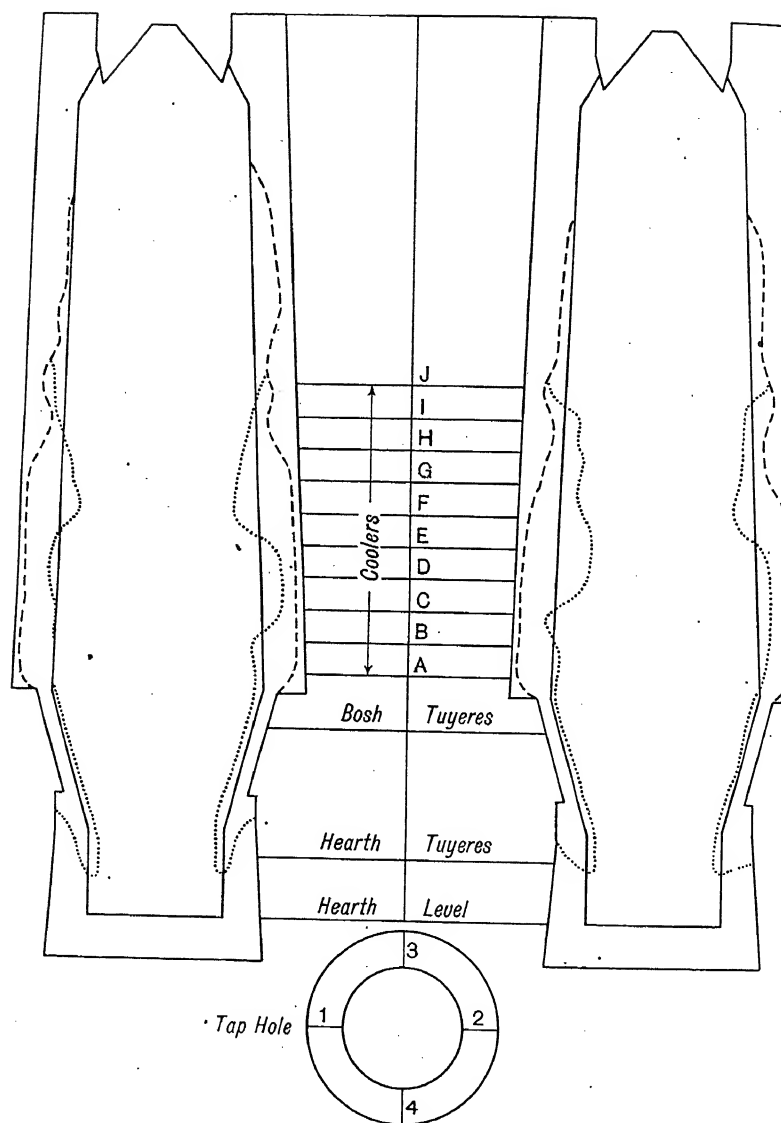— — — — — — — Remaining brickwork.

Fig. 36.—Sections through furnace showing original lines and lines after blowing out : section 1, 2 on the left ; section 3, 4 on the right.

—— Original brickwork.
... Scar.
.— — Remaining brickwork.

was computed that over 6 in. of the brickwork disappeared during the first six weeks of the working of the furnace. Temporary scars which slowly built up and then apparently fell away were a normal feature in the bosh region. While this scar formation was no doubt important in serving as a protection for the permanent lining, it appeared to affect the working of the furnace adversely. A large quantity of limy accretions suddenly deposited in the hearth may cause severe chilling, resulting in the production of off-grade iron. The slope of the bosh in relation to the other dimensions of the furnace probably has a determining influence on the rate at which these scars form and the thickness they can attain.

### (d) The Hearth.

In the lining extending between the tuyere level and hearth bottom, W. Woodhouse, W. Hugill, and A. T. Green [13] reported vitrification and penetration both of iron and slag in the front portion of the lining. The present authors investigated the bricks taken from the bed of the hearth in a furnace which had suffered six breakouts. An inspection of the hearth revealed a channel in the brickwork which had been cut out by the molten iron, and there was no sign of a coke-tar bed which had been rammed on top of the hearth bricks to a depth of 2 ft. Around this channel the bricks had been displaced and were out of alignment. Iron had forced its way between the joints, which had opened in some cases to a width of 2 in. There appeared to be no corrosion of the bricks by the iron, but the texture of the brickwork ·had been profoundly modified. The bricks were now slate grey in colour, had no porosity, and were extensively vitrified under the combined effects of pressure and temperature to a texture resembling that of stoneware. Many bricks showed extensive spalling, and iron had penetrated in some cases to the centre of the brick by means of these spalling cracks.

### III. Laboratory Investigations on the Durability of Blast-Furnace Linings.

### (a) The Action of Carbon Monoxide on Refractory Materials.

The action of carbon monoxide on refractory materials has been investigated in the laboratory by numerous workers. There is general agreement that deposition of carbon occurs most rapidly over the temperature range 450°–500° C., although according to S. M. Phelps [20] the reaction $2CO \rightarrow CO_2 + C$ begins at 300° and continues up to 525° C.

The influence of the texture of the refractory material has been investigated by W. Hugill, H. Ellerton, and A. T. Green,[21] who contrasted the permeability of a number of fireclay specimens with resistance to carbon monoxide disintegration. They concluded that other factors completely overshadowed any variation due to differences in permeability.

There is general agreement that the ferruginous matter usually found in fireclay materials is of considerable importance in determining the extent of carbon deposition, although W. Hugill and A. T. Green [22] could not correlate the total iron oxide content as determined by analysis with the resistance offered to disintegration. They were able to differentiate, however, between two types of iron spots. In bricks which were disintegrated the iron spots contained a blue-black crystalline material, which had a higher density than 2·95. By means of flotation in bromoform they were able to isolate a quantity of these blue-black crystals and to demonstrate that they were particularly active in promoting deposition of carbon. The investigators [23] next prepared specimens containing definite amounts of added hæmatite, magnetite, pyrites, and an artificial iron oxide–clay fusion. The hæmatite addition produced the most rapid disintegration, while the iron oxide–clay fusion was the least effective.

As blast-furnace gas contains between only 25 and 35 per cent. of carbon monoxide, the effect of concentration has to be considered. W. Hugill and A. T. Green [24] using carbon monoxide diluted with nitrogen showed that while the rate of disintegration is slower with the diluted gas, those materials which fail in pure carbon monoxide will also fail ultimately when the proportion of carbon monoxide is reduced.

R. P. Heuer [25] suggested that prevention of disintegration might be attained if the iron compounds in the refractory material could be induced to enter into combination with the clay material. In support of this, W. Hugill and co-workers showed that a high temperature in the firing of fireclay materials, particularly in a reducing atmosphere, caused a marked reduction in the tendency for disintegration to occur. They did not, however, consider that it was always feasible to increase the final temperature of firing to such a degree that the iron compounds were rendered innocuous, since the possibility of other detrimental results of excessive firing must not be overlooked. The Farbenindustrie [26] claimed that refractory materials could be rendered immune from disintegration by impregnating the bricks with a dilute solution of copper sulphate. There appears to be only one definite way in which the tendency for a material to disintegrate can be assessed, and that is by subjecting it to the action of carbon monoxide in a standard laboratory test.

### (b) The Action of Alkalies on Refractory Materials.

The sources of alkali in the blast-furnace are mainly found in the coke and the ore. These alkalies are only partially removed by the slag, so that the tendency is for the alkali salts to accumulate. It has been demonstrated by several investigators [27] that sodium chloride at 800° C. is hydrolysed by water vapour to give caustic

soda and hydrogen chloride.   The presence of alkali hydroxides, carbonates and cyanides in blast-furnace linings can thus be readily accounted for.   The fluxing actions of soda and potash have been investigated by A. S. Watts.[28]   His conclusions were that when the alumina-silica ratio exceeded that of the kaolin formula ($Al_2O_3 : SiO_2$ as 46 : 54) potash and soda were more severe fluxing agents than lime and magnesia, but as the proportion of silica to alumina increased the reverse became true.   R. J. Montgomery and C. E. Fulton [29] concluded, however, that materials with a silica to alumina ratio of 84 : 16 were most susceptible to the action of fluxing oxides.

It has been shown from a consideration of blown-out linings that alkalies may attack the lining when in the solid, liquid, or gaseous states.   J. W. Cobb [30] has drawn attention to the large forces attending the crystallisation of some salts irrespective of whether there is an expansion or contraction on crystallisation ; thus disruption of brickwork may be consequent upon crystallisation of salts.

D. Turner and W. E. S. Turner,[31] investigating the corrosive effects of molten sodium and potassium carbonates, nitrates, and sulphates, came to the conclusion that the physical texture of the fireclay material was of greater importance than its chemical constitution in controlling the rate of attack.   These investigators also found that the same clay fired at 1,400° C. was more resistant than when fired at 1,300° C.

The action of alkalies in the vapour phase has been studied mainly by F. H. Clews and A. T. Green.   In the preliminary investigations the absorption of potash vapour at 900° C. and 1,000° C. was investigated.[32]   The absorption was found to be greatest with an aluminous material which on continued exposure to alkali vapour mechanically disintegrated.   An external viscous silicate formed on the other fireclay specimens and appeared to act in a protective manner.   The extent of chemical decomposition was determined by treatment, after absorption, with dilute hydrochloric acid and weighing the undecomposed residue.   The conclusions were that within the range of temperature investigated, refractories approximating in composition to a normal fireclay are likely to resist free alkali vapour more effectively than either more aluminous or siliceous materials.

The work was further extended to the action of the vapours of alkali chloride at 1,000° C.[33]   The action of potassium chloride vapour was different from that of the hydroxide because of the ability of the chloride to penetrate within the brick structure before reacting chemically.   Siliceous firebricks were found to be less reactive to potassium chloride vapour than normal fireclay products, but more reactive than aluminous fireclay materials.   After exposure to potassium chloride vapour it was found that the fireclay specimens had increased in size without any distortion occurring.[34]   In practice this might lead to disruptive stresses of a high order.   A

second feature accompanying the exposure of refractory materials to potassium chloride vapour was the migration of iron oxide from the interior to the exterior of the specimen.    Later it was found that some volatilisation of iron from the specimen could also occur.[35] The surface deposit produced using alkali chloride vapour and dry air was found to be reactive with carbon monoxide at 400° C., surface growths of carbon being formed.    Disruption of the specimen was not obtained, due no doubt to the location of the iron compound on the surface, but the specimens parted from the cement by means of which they were initially fixed to a refractory plaque.    A third result of interest was the decrease in mechanical strength which occurred both at room temperature and 1,000° C. when fireclay specimens were exposed to the vapour of potassium chloride.[36]

### (c) The Action of Slags on Refractory Materials.

The literature with regard to the action of slags is voluminous, but of particular moment with regard to blast-furnace refractories is the work of W. Hugill and A. T. Green.[37]   Four blast-furnace finishing slags were selected having the analyses given in Table XXV. Slags II and III were largely composed of gehlenite, while slag IV contained a preponderance of calcium orthosilicate.    Among the refractory materials studied were a highly aluminous brick, aluminous, ordinary, and siliceous firebricks.   Three methods of testing were applied to study the corrosive action of the slags.    In the first method the refractoriness of a range of mixtures of powdered slag and brick was determined.    The second method consisted of measuring the extent of corrosion and penetration of the slag into the brick when a compressed cylinder of powdered slag was melted on the upper surface of the brick.    The third method was concerned with the extent of erosion obtained by injecting powdered slag into the air blast of a flame which impinged on the vertical face of the hot specimen.   The refractoriness curves obtained by the first method could be correlated with certain features in the ternary lime–silica–alumina phase-rule diagram.    A noticeable feature in all curves was a relatively low minimum temperature of softening, varying only between 1,140° and 1,200° C. despite the wide variation existing in the composition of the refractories.   In the second method interaction involving liquefaction occurred between the slag and brick at the temperature of minimum melting.    Examination of the crystallised products has shown in most cases the presence of anorthite formed by the action of liquid slag on the brick.    The residual melt then penetrated further into the brick and conduced to the formation of mullite in all but the most siliceous products. On the basis of the depths of corrosion and penetration, indications of an order of merit in the alumina and fireclay materials were obtained.    The slags approaching calcium orthosilicate in constitu-

tion, and consequently of a more calcareous nature than the remaining two, were also more corrosive.   The presence of anorthite as an end-product of the reaction also indicated that lime could be regarded as the essential corroding agent.

TABLE XXV.—ANALYSES OF SLAGS.

|  | Slag I. | Slag II. | Slag III. | Slag IV. |
|---|---|---|---|---|
| SiO₂ per cent.  .. | 27·33 | 32·52 | 25·31 | 32·59 |
| Al₂O₃  ,,  .. | 21·08 | 21·29 | 27·90 | 9·35 |
| CaO  ,,  .. | 47·91 | 44·06 | 37·17 | 56·87 |
| MgO  ,,  .. | 2·46 | 1·57 | 5·24 | 1·77 |

The same investigators next examined the corrosive action of lime alone, using the second method of slag testing.[38]   The results indicated that the corrosive action of pure lime was more pronounced than with the blast-furnace slags.   The depths of corrosion of seven of the ten refractory materials investigated were found to be inversely proportional to their respective alumina contents.   These observations accorded with the work of J. R. Rait and R. Hay [12] who found that the viscosity of lime–silica–alumina slags having a constant $CaO : SiO_2$ ratio increased with the alumina content when this exceeded 17 per cent.

It is obvious that the methods as used by A. T. Green and W. Hugill could not give a complete picture of the action of slags in the blast furnace.   Their methods emphasised the chemical attack of the slag, but in practice this effect is modified by the melting-points and viscosities both of the slag and its intermediate compounds owing to the temperature gradients which exist within the lining.   Although lime is essentially the agent which causes corrosion, slags high in lime are often more viscous than those with a lower $CaO : SiO_2$ ratio, and this increased viscosity modifies the potential increase in corrosive power due to the higher lime content. It is generally recognised that akermanitic slags are more severe on the lining than slags of the gehlenitic type, owing to the former having a lower viscosity.

IV. THE CHOICE OF REFRACTORY MATERIALS FOR THE LINING.

(a) The Brickwork.

According to the questionnaire circulated to blast-furnace plants in 1931, it appeared that the refractories were generally obtained from firms within reasonable distance from the plants. Thus it was found that a wide range of products were used for the linings, varying in composition from 75 per cent. $SiO_2$ and 20·13 per cent. $Al_2O_3$ to 48·70 per cent. $SiO_2$ and 46 per cent. $Al_2O_3$.   The information received gave no guide as to whether the aluminous or

9

siliceous type of firebrick was more durable in the lower regions of the furnace. Nevertheless during the last decade three distinct tendencies can be observed, particularly in German and American practice. First the substitution of smaller machine-pressed units for the large hand-made blocks is finding favour ; secondly, bricks with a close texture are receiving preference ; and thirdly, there is a tendency to use firebricks of the aluminous variety in the hearth and bosh. Among the properties of the refractory materials which should receive careful consideration are the following : (1) chemical composition ; (2) refractoriness and refractoriness-under-load ; (3) after expansion or contraction ; (4) permeability and porosity ; (5) resistance to carbon monoxide disintegration ; (6) resistance to abrasion ; (7) accuracy of shape.

With regard to chemical composition J. G. West [39] has stated that in the U.S.A. a 43 per cent. alumina brick is favoured for the hearth and bosh regions and a 39 per cent. alumina brick for the stack. M. Barrett [40] has also drawn attention to the tendency for a 40 per cent. alumina material to be used in America and Germany and he contrasted this with the use of a 30 per cent. alumina material as used in England. According to W. J. Rees [41] laboratory tests indicated that aluminous bricks were more resistant to corrosion both by slags and absorbed alkalies than were siliceous bricks.

According to A. T. Green and W. Hugill [42] all lining materials should satisfy the requirements of good fireclay refractories having adequate refractoriness and a low after-contraction at 1,350° or 1,400° C. J. H. Chesters and T. W. Howie,[43] while giving tentative specifications, suggested the following minimum requirements : refractoriness, cone 30 ; refractoriness under a load of 50 lb. per sq. in., 1,340° C. ; and change in length after heating for 2 hours at 1,410° C., $\pm 1 \cdot 3$ per cent. It is obvious that the high temperatures experienced in the bosh and hearth regions do not admit of the use of firebricks having a refractoriness value below cone 30. A low after-expansion or contraction necessitates the use of well-fired products. Any shrinkage of the lining bricks when in position results in the opening up of the joints and exposes the lining behind the working face to attack by alkali vapours and carbon monoxide. Particular attention should be paid to the after-contraction properties of hearth bricks, as open joints appear to be the first stage towards a hearth breakout.

A criterion of texture and resistance to abrasion may be obtained from the porosity, permeability, and cold crushing strength of the refractory materials. A close texture tending to give resist

aking.
that increasing the
increases the crushing
while decreasing the

refractoriness-under-load values
According to one report [44] a

general recommendation is that all grog should pass a $\frac{1}{8}$ in. diameter and be retained on a 50 mesh. The tendency, particularly in America, has been to use high moulding pressures. R. Sweetser [45] mentioned the use of making pressures up to 3,500 lb. per sq. in. on materials with low moisture contents, and V. Rybnikov [46] has used pressures as high as 8,750 lb. per sq. in. Bricks both pressed and de-aired are also finding favour in America for stack linings. R. A. Lindgren [47] stated that de-airing has improved blast-furnaces bricks to a great degree, J. S. McDowell [48] found that evacuation prior to pressing produced bricks of low porosity, and A. V. Leun [49] reported that de-aired bricks have been used in blast-furnaces with good success. The following Table given by J. G. West [39] illustrates very well the modern American tendency for bricks of lower porosity:

TABLE XXVI.—DATA DUE TO J. G. WEST.[39] POROSITIES OF BLAST-FURNACE BRICKS.

| Position. | Hand Made, 1920. | Power Pressed, 1930. | Power Pressed —De-aired, 1937. |
|---|---|---|---|
| Hearth and Bosh .. .. | 24·0 | 21·1 | 16·0 |
| Inwall .. .. .. | 22·0 | 19·0 | 15·0 |
| Top .. .. .. | 21·0 | 18·2 | 14·0 |

It has been shown in the laboratory that the total iron content of a clay is no safe criterion in assessing the resistance of refractory materials to carbon monoxide disintegration, as the way in which the iron is combined is the most important factor. Firebricks for stack linings should therefore be subjected to a test which is capable of measuring the resistance to carbon monoxide, and representative specimens taken from both the surface and interior of the firebrick should be maintained at 450° C. in an atmosphere of carbon monoxide. Materials which remain unchanged after 200 hours exposure might be considered to have passed this test. Since it has been shown that a high firing temperature is indicative of resistance to carbon monoxide disintegration, small blocks are preferable to the old type of hand-made blocks which are difficult to fire uniformly. An exception might be made here in favour of the large blocks containing upwards of 90 per cent. grog which have been used mainly on the Continent. As these bricks contain a high proportion of prefired material, the resistance to carbon monoxide is largely dependent on the initial burning of the grog rather than on the firing of the block itself.

(b) *The Cement.*

The penetration of gases, vapours, and slags into the lining is effected largely by passage through the joints. The choice of a

suitable cement is attended by difficulties, and it is for this reason that every endeavour is now made to reduce the width of the joints to a minimum by employing brick shapes which are true to size and give a close fit.  A cement is required which does not contract in use and it should, therefore, contain a high proportion of non-plastic material.  The cement, however, should also have low permeability. This suggests the formation of a vitrifiable bond at the temperature to which it is subjected.  It has been pointed out by A. Stein that the temperature of the bricks at the throat is too low to enable a vitrified bond to form when a fireclay-fireclay grog cement is used. He therefore suggested that in the throat brickwork an air-setting cement should be employed.  This might advantageously be extended to the cooler brickwork nearest to the stack casing in the whole shaft.

*(c)  The Packing between Brickwork and Casing.*

It is essential to pack the space between the casing plates and brickwork with some compressible material.  This material gives support to the brickwork when expanding, and also retards the flow of gas through the actual lining.  In this country slag wool is commonly used, but other products recommended are diatomaceous earths and granulated carbon.  The use of granulated carbon [50] is an attempt to keep the temperature gradient through the lining as steep as possible, thus reducing the width of the zone liable to carbon monoxide penetration to a minimum.  Diatomaceous earth, on the other hand, is a poor conductor of heat, consequently the gradient through the lining is reduced.  With a working-face temperature of 800° C. the cold face of a 3-ft. lining could be maintained at 600° C. by placing about 9 in. of insulating material between brickwork and casing.  Thus the whole of the lining is above the temperature for optimum disintegration by carbon monoxide.  However, with a working-face temperature of 600° C. and using a similar thickness of insulating materials, the cold face temperature is in the region of 450° C. and in consequence the whole of the lining is in the temperature range for effective disintegration by carbon monoxide.  This suggests the necessity for a knowledge of the temperature gradients through the lining and of the effect of insulation on the temperature gradient, before insulation is adopted.

*(d)  The Water Cooling of Blast-Furnace Stacks.*

The authors have obtained continuous records of the temperatures in three planes of a blast-furnace stack cooled by the insertion of cast-iron cigar coolers.  They have been able to compare these temperatures with those obtained in a blast-furnace stack which was not water cooled.  As this investigation is still continuing it would be inadvisable at this stage to report detailed observations. Both furnaces were identical in that similar burdens were used,

throat and bell diameters were the same, and there was no deviation in the mechanism of burden distribution. The segregation of the burden in each blast-furnace might be considered, therefore, to be comparable. The water-cooled stack, however, had a slightly increased batter which was reflected in that furnace driving much better than the corresponding one containing no stack cooling. Both furnaces were lined with the same quality of firebricks. Two important points soon emerged from this investigation : first, the temperatures recorded in both stacks were of the same order and secondly the rate of wearing back of the lining during the first six months of the campaign was greater with the stack containing no water-coolers. The couples in the water-cooled stack were placed equidistant between the coolers on each side. The tip of the thermocouple which terminated 6 in. behind the working face was thus the maximum distance (18 in.) away from the nearest coolers. The temperatures recorded suggested that the tip of the thermocouple was outside the range of water cooling. On the other hand, a thermocouple placed directly below a copper bosh cooler was found to record a temperature approximately 150° C. lower than similar couples placed in the same plane but equidistant between two cooler blocks. This suggests the presence of temperature gradients radial to the cooler blocks, but the cooling influence in the stack could not be detected at a distance of 18 in. from the cooler surface. In a water-cooled stack, therefore, there is a much steeper temperature gradient normal to the working face directly in front of a cooler than there is at positions equidistant between two coolers.

After 6 months in blast there was no evidence that the lining in the water-cooled stack had worn back. It was estimated that the corresponding stack containing no coolers lost at least 6 in. of lining at positions 23 ft. below the stock line after being in blast for six months. It is difficult to ascribe the difference in the wearing back of the two linings to factors other than the water cooling. It would appear, therefore, that stack cooling is likely to be beneficial to lining life, particularly with those furnaces where the gas velocity is a maximum in the peripheral layers of the stock column. The variations recorded by all couples in both furnaces could be satisfactorily correlated with the porosity of the stock column. A change of burden resulting in a more porous stock column, either by the inclusion of more coke or ores containing less fines, resulted in a decrease in the stack temperatures. This was no doubt due to a larger proportion of the gases passing up the centre of the stock relative to the sides.

(e) *The Hearth.*

When fireclay blocks are used for the hearth particular attention must be paid to the joints, to ensure that they are as close as possible and are broken at each course. A bed of coke and tar rammed on

top of the brickwork is stated to be impervious to the metal, but care must be taken during the blowing-in of the furnace to preserve the coke-tar bed from burning away. In Germany the carbon hearth is much favoured and appears to be very successful. According to F. Clements,[51] F. Singer [52] and others, the lining must be protected during the blowing-in period by a temporary covering of fireclay slabs which are corroded away when the hearth receives metal and slag. A plated bosh is preferred in connection with the carbon hearth, to prevent the ingress of air. According to F. Singer, German carbon blocks have an ash content which does not exceed 10 per cent., the compressive strength is about 1,710 lb. per sq. in., the total porosity 30–35 per cent. and the apparent specific gravity 1·35. A carbon block made in Germany and tested by the authors had the following properties : ash content 5·61 per cent., apparent porosity 30·3 per cent., apparent specific gravity 1·33 per cent., and cold crushing strength 2,220 lb. per sq. in. F. J. Vosburgh [53] reported that 75 per cent. of all blast furnaces in Germany are carbon lined, one furnace claimed to have made 2,000,000 tons of iron and other furnaces are expected to exceed this figure.

*(f) The Blowing-in of the Lining.*

The first consideration when a new lining is installed is to dry it out. In the case of the hearth brickwork this is best effected by drying successive courses during the building, as a fire built on the hearth probably does not completely dry the lower courses. If this is the case, when the furnace is blown-in there is a possibility of steam being generated with sufficient violence to displace the hearth brickwork in the top courses, and to make a channel for the iron to penetrate through the brickwork.

After the drying-out period the furnace is generally blown-in by feeding with wood followed by skips of coal or coke gradually changing to a light burden, and after an interval of two to three days the first tap of iron is made. Data on the lining temperatures recorded during the blowing-in period have not been reported, but the authors are responsible for the figures quoted in Table XXVII, which were recorded by thermocouples placed 6 in. behind the working face.

As may be seen from Table XXVII, the temperatures in the bosh and lower stack began to rise when blast was introduced through the tuyères. The rise in temperature of the bosh couples averaged 14° C. per hour until the temperature of 1,000° C. was recorded 6 in. behind the working face, corresponding to an actual face temperature of approximately 1,400° C. At certain periods, however, the temperature rise was greatly in excess of this figure. When the furnace began to drive on the ordinary burden all temperatures decreased to a steady value.

TABLE XXVII.—BLOWING-IN TEMPERATURES OF A FURNACE.

*Furnace A.*

| Hours. | 9 ft. above Tuyères. | 17 ft. above Tuyères. | Remarks. |
|---|---|---|---|
| 0 | 90° C. | 75° C. | Timber, coal, and coke charges. |
| 20 | 65° C. | 75° C. | |
| 30 | 70° C. | 75° C. | Furnace full—0·2 lb. blast. |
| 40 | 530° C. | 130° C. | Blast increased to 3·3 lb. in stages. |
| 50 | 870° C. | 420° C. | First tap of iron. |
| 60 | 1,000° C. | 670° C. | — |
| 100 | 1,020° C. | 950° C. | Blast increased to 4·5 lb. in stages. |
| 120 | 950° C. | 900° C. | |

In the section concerned with the properties of lining bricks the growing tendency to use bricks of low porosity was commented upon. These bricks, while more resistant to gas penetration and slag attack, may be expected to be sensitive to thermal spalling. The figures in Table XXVII indicate that unless the blowing-in period is very carefully controlled severe spalling of the brickwork may occur, particularly if a dense product is used. In comparison with other installations the blowing-in periods for blast-furnaces generally appear much too rapid to ensure complete immunity from spalling although it is difficult to assess the extent of damage which occurs during this period.

REFERENCES.

1. British Iron and Steel Federation. Reports upon Blast Furnace Field Tests (2).
2. *Iron and Steel Institute, Special Report No.* 18, 1937.
3. S. P. Kinney, R. H. Royster, and T. L. Joseph, *U.S. Bur. of Mines Tech. Paper No.* 391, 1927.
4. S. P. Kinney, *Blast Furnace and Steel Plant,* **22**, 152, 209, 1934.
5. H. W. Johnson, *ibid.,* **26**, 165, 590, 689, 1938.
6. A. T. Green and W. Hugill, *Bull. B.R.R.A.,* **30**, 55, 1933.
7. F. Clements, "Blast Furnace Practice," Vol. 2, p. 150.
8. S. P. Kinney, *U.S. Bur. of Mines Tech. Paper No.* 397, 1926.
9. C. D. Abell, *Ind. Chemist,* **8**, 110, 128, 191, 1932.
10. R. S. McCaffery, *Amer. Inst. Min. Met. Eng.,* Tech. Pub., 383, 1931.
11. T. P. Colclough, *J. Iron and Steel Inst.,* **134**, 547, 1936.
12. J. R. Rait and R. Hay, *J. Royal Tech. Coll., Glasgow,* **4**, (2), 252, 1938.
13. W. Woodhouse, W. Hugill, and A. T. Green, *Bull. B.R.R.A.,* **45**, 45, 1938.
14. F. Hartmann, *Stahl Eisen,* **52**, 1060, 1932.
15. B. Osann, "Lehrbuch der Eisenhüttenkunde," Band I, 639.
16. W. Feldmann, *Stahl Eisen,* **52**, 1290, 1932.
17. F. H. Clews and A. T. Green, *Bull. B.R.R.A.,* **30**, 273, 1932.
18. C. L. Beattie, *Iron & Coal Trades Review,* **124**, 273, 1932.
19. A. T. Green, W. Hugill, and H. Ellerton, *Bull. B.R.R.A.,* **31**, 36, 1933.

20. S. M. Phelps, *J. Amer. Ceram. Soc.*, **7**, 716, 1924.
21. W. Hugill, H. Ellerton, and A. T. Green, *Bull. B.R.R.A.*, **26**, 37, 1931; *Trans. Ceram. Soc.*, **32**, 543, 1933.
22 W. Hugill, H. Ellerton, and A. T. Green, *Bull. B.R.R.A.*, **25**, 14, 1931; *Trans. Ceram. Soc.*, **32**, 533, 1933.
23. W. Hugill, H. Ellerton, and A. T. Green, *Bull. B.R.R.A.*, **28**, 64, 1932.
24. W. Hugill, H. Ellerton and A. T. Green, *ibid.*, **32**, 43, 1933.
25. R. P. Heuer, *J. Amer. Ceram. Soc.*, **12**, 30, 1929.
26. *Tonind. Ztg.*, **55**, 470, 1931.
27. J. W. Cobb, *Gas World*, p. 11, April, 1916.
28. A. S. Watts, *J. Amer. Ceram. Soc.*, **6**, 1150, 1923.
29. R. J. Montgomery and C. E. Fulton, *Trans. Amer. Ceram. Soc.*, **9**, 303, 1917.
30. J. W. Cobb, *ibid.*, **11**, 65, 1909.
31. D. Turner and W. E. S. Turner, *J. Soc. Glass. Tech.*, **7**, 207, 1923.
32. F. H. Clews, A. Green, and A. T. Green, *Bull. B.R.R.A.*, **32**, 1, 1933.
33. F. H. Clews, A. Green, and A. T. Green, *ibid.*, **35**, 22, 1934.
34. F. H. Clews, H. M. Richardson, and A. T. Green, *ibid.*, **41**, 33, 1936.
35. F. H. Clews, H. M. Richardson, and A. T. Green, *ibid.*, **48**, 1, 1938.
36. F. H. Clews, H. M. Richardson, and A. T. Green, *ibid.*, **48**, 12, 1938.
37. W. Hugill and A. T. Green, *ibid.*, **42**, 35, 1937.
38. W. Hugill, R. L. Ainsworth, and A. T. Green, *ibid.*, **47**, 10, 1938.
39. J. G. West, *Blast Furnace and Steel Plant*, **26**, 77, 183, 290, 1938.
40. M. Barrett, *ibid.*, **21**, 123, 1933.
41. W. J. Rees, *Refract. J.*, **11**, 423, 1935.
42. A. T. Green and W. Hugill, *Bull. B.R.R.A.*, **30**, 55, 1933.
43. J. H. Chesters and T. W. Howie, *Trans. Ceram. Soc.*, **38**, 131, 1939.
44. *British Clayworker*, **37**, 258, 1928.
45. R. Sweetser, *Min. and Met.*, **13**, 319, 1932.
46. V. Rybnikov, *Steel*, **11**, 95, 1936.
47. R. A. Lindgren, *Brick*, **91**, 38, 1937.
48. J. S. McDowell, *Refract. J.*, **14**, 121, 1938.
49. A. V. Leun, *Iron and Steel Eng.*, **14**, 41, 1937.
50. Y. Kirakawa, *Suiyokwai-Shi*, **9**, 425, 1938.
51. F. Clements, " Blast-Furnace Practice," Vol. 2, 141.
52. F. Singer, *Metals and Alloys*, **10**, 104, 1939.
53. F. J. Vosburgh, *ibid.*, **10**, 133, 1939.

# (5) Temperature Gradients through Blast-Furnace Linings.*

## Part. I.—An Investigation of a Furnace not Fitted with a Stack Cooling System:

By G. R. Rigby, Ph.D., B.Sc., A.R.C.S., D.I.C., A.I.C.,
H. Booth, and A. T. Green, F.I.C.

Abstract.

An attempt has been made to assess the rate at which a blast-furnace lining wears back by inserting thermocouples in five planes in the stack and bosh and taking continuous records of the temperatures. The results indicated the formation and subsequent removal of temporary scars in the bosh region. The temperature records in the stack have been correlated with variations in the flow of the blast through the stack due to burden changes. The computed furnace lines at the end of the campaign compare satisfactorily with the lines as actually measured. It is considered possible from such temperature data to obtain an estimate of the lines of the furnace at any particular time during a campaign. In an appendix the effect of segregation of the burden on the life of the lining is treated in a general manner.

## I. Introduction.

A number of the factors which promote the failure of blast-furnace linings are now generally appreciated. They include disintegration of the brickwork by carbon monoxide, and corrosion by alkali vapours and calcareous slags. Examinations of blown-out linings supplemented by special laboratory investigations have done much to reveal the conditions under which disintegration of fire-brick materials can occur. As a result it is now generally recognised that aluminous products offer greater resistance to slag and alkali attack, while a high firing temperature tends to increase the resistance of firebricks to carbon monoxide disintegration.

It appears unlikely, however, that a complete appreciation of the problem of the durability of blast-furnace linings can be obtained solely by considering the lining at the end of a campaign. Data are also urgently required which will throw light on the rate at which the lining wears back during the furnace campaign. There is also a singular lack of definite information concerning the conditions imposed on the lining during use. The authors have already drawn attention to the wide variations in inwall stack temperatures which have been reported for a number of blast furnaces, and have emphasised that the durability of a lining is intimately bound up with

* *Bull. B.R.R.A.*, **58**, 1, 1941.

the way in which a furnace is driven.[1]   Many data have been compiled on the contours of blown-out furnaces, since most firms record their blowing-out lines.   On the other hand, there is little information on the manner in which the lines of the furnace continually vary during a campaign.   There has long been an opinion that during the first few weeks of blowing-in, a furnace rapidly alters its lines to the most suitable contours, but in the absence of any definite evidence such assumptions remain purely conjectural.   In practice it is considered very desirable to try to retard the wearing-back in the bosh region by means of water cooling, either by the insertion of cooler blocks or by the use of an external spray.   On the Continent, this application of water cooling has spread to the whole of the furnace lining, and furnaces have been described in which extensive stack cooling systems have been utilised in conjunction with a refractory lining only 2 ft. thick.[2]   Data which could be used to assess the influence of stack coolers on the rate at which the lining wears back would be of great service in appraising the merits of water cooling generally.

The present investigation is an attempt to throw light on some of these problems by taking continuous measurements of temperatures inside the furnace lining during an entire campaign.   The authors have been fortunate in obtaining permission to collect data both from a furnace without stack cooling and from a second furnace with coolers in the stack.   The investigation on the second furnace is still continuing, so that the conclusions relating to the efficacy of water-cooling must serve as the basis of a later paper.   This report is concerned with the data obtained from a furnace which was without a stack-cooling system.

## II.  Description of the Furnace and its Working.

(a)  *Furnace Lines.*

The lines of the furnace prior to blowing-in are given in Fig. 37 ; details of the furnace were as follows :—

| | |
|---|---|
| Height from hearth to top of stack | 72 ft. 3 in. |
| Height of stack    .. | 52 ,, 9½ in |
| Height of bosh    .. | 12 ,, 5½ ,, |
| Diameter of throat | 14 ,, 3  ,, |
| Diameter of bosh .. | 16 ,, 0½ ,, |
| Diameter of hearth | 10 ,, 6  ,, |
| Bosh angle    .. | 77° 27′ |
| Diameter of bell  .. | 8 ft. 6 in. |

(b)  *Tuyeres.*

There were 8 hearth tuyeres, one directly over the tap-hole of 3 in. diameter (Jumbo tuyere), the others being of 6 in. diameter, when the furnace was in full blast.
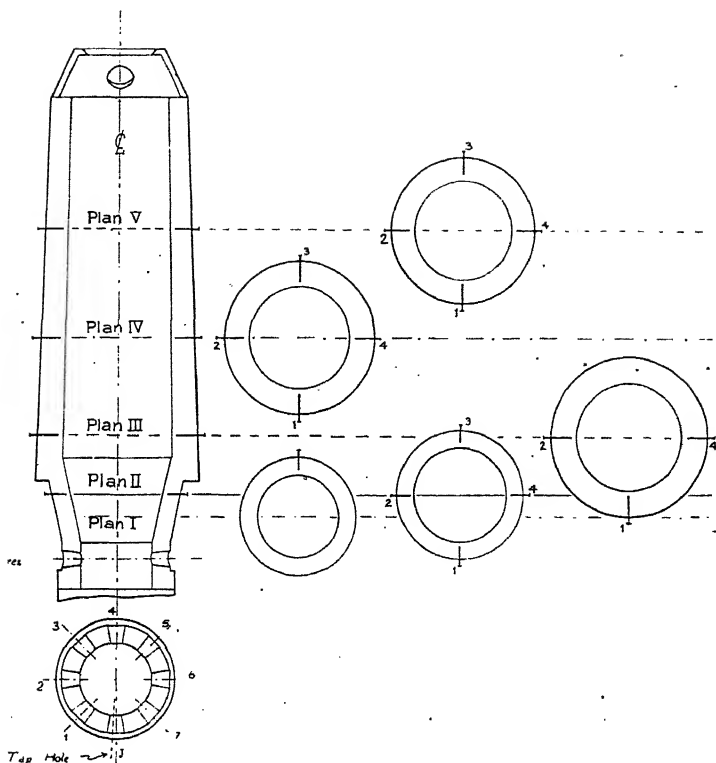
Fig. 37.—Blast furnace lines and dispositions of the thermocouple planes.

(c) *Cooling*.

Copper blocks were inserted only in the bosh which was of the banded type and continued for a distance of 4 ft. above the lintel plate. There were sixteen cooler blocks in each of 12 rows with the exception of the two rows at the tuyere level, where 8 coolers alternated with the 8 tuyeres.

(d) *The Lining*.

The stack and bosh linings comprised bricks of dimensions $13\frac{1}{2}$ in. $\times$ 6 in. $\times$ 3 in. and 9 in. $\times$ 6 in. $\times$ 3 in. with the corresponding tapers. The bricks were set with dipped joints. The bricks for the bosh and stack were of different brands having the following reported properties : stack bricks, percentage analysis : $SiO_2$, 61·59 ; $Al_2O_3$, 35·33 ; $Fe_2O_3$, 2·50 ; $TiO_2$, 1·20 ; $CaO$, 0·20 ; $MgO$, 0·30 ; $K_2O$, 1·30 ; $Na_2O$, 0·10 ; refractoriness : cone 32. Bosh bricks, percentage analysis : $SiO_2$, 53·51 ; $Al_2O_3$, 42·44 ;

$Fe_2O_3$, 2·60 ; $TiO_2$, 1·10 ; CaO, 0·40 ; MgO, 0·50 ; $K_2O$, 0·10 ; $Na_2O$, trace ; refractoriness, cone 34–35. In addition both grades of brick resisted disintegration by carbon monoxide on exposure for 200 hours at 450° C. The thickness of the lining in the bosh was 2 ft. 7½ in. ; in the top third of the stack, 3 ft. ; in the middle third, 3 ft. 4½ in. ; and in the lower third 3 ft. 9 in. The top 3 ft. of the throat was protected by a row of steel plates fastened into the brickwork. The space between the lining and casing was packed with granulated blast-furnace slag. The tap-hole was 5 ft. 6 in. below the centre line of the tuyeres, facing due west, and the slag notch was 2 ft. 3 in. below the centre line of the tuyeres, making an angle of 63° with the tap-hole towards the south.

### (e) *The Burden and Types of Iron made.*

The furnace was mechanically charged by means of a bucket which rotated when receiving the loads. The bucket was then elevated vertically to the height of the furnace, and picked up by a carriage which carried it horizontally over the bell. The distributing mechanism consisted solely of this rotating bucket and the single bell.

Table XXVIII gives the ores used in the burden, their iron contents and a rough estimate of the fines in each ore passing a ½-in. sieve.

TABLE XXVIII.—DESCRIPTION OF THE ORES.

| Mark. | Ores. | Fe Content (Per Cent.). | $SiO_2$ Content (Per Cent.). | Percentage passing a ½-in Mesh. |
|---|---|---|---|---|
| R | N. Staffs calcined | 56·5 | 5·2 | 30 |
| I | Northants | 44·0 | 9·5 | 60 |
| O | Oxfordshire | 27·0 | 10·0 | 50 |
| P | Swedish .. | 57·0 | . | 40 |
| L | South Wales | 50·0 | 5·5 | 75–80 |
| H | African .. | 55·0 | | 40 |
| T | Flue cinder | 50·0 | 15·0 | 25 |
| S | Basic slag | | 10 | |

The ores were not graded in any way but stored in large bunkers. As segregation of each ore occurred in the bunkers, only a qualitative estimate of the amount of fines in the burden could be formed. The Northamptonshire ore in particular was very variable in size, pieces weighing well over 60 lb. were present as well as a large percentage of fine material.

The coke was obtained exclusively from one source ; nevertheless, it varied from time to time. The coke for each charge was screened through bars before elevating it into the furnace. This screening operation did not, however, remove all breeze.

The limestone was generally obtained from Derbyshire, and contained 97·5 per cent. $CaCO_3$.

The furnace was blown-in on December 8th, 1938, and after a period of intermittent working was damped down on January 28th, 1940. During this period two types of iron were made, basic iron with an average analysis : silicon, 0·5–1·5 per cent. ; sulphur, 0·05 per cent. ; phosphorus, 1·8 per cent. ; manganese, 2·0 per cent. ; and foundry iron which had an average analysis of : silicon, 1·0 per cent. ; sulphur, 0·04 per cent. ; phosphorus, 0·8 per cent. ; and manganese, 1·5 per cent.

### (f) *Details of the Furnace when in Blast.*

During the campaign of sixty weeks the furnace gave a great deal of trouble due to hanging of the burden. This tendency was particularly prevalent in the early stages of the campaign but improved somewhat as the lining wore to more suitable contours. The difficulty in obtaining free movement of the stock could probably be ascribed to the negligible batter on the stack which was only 1 in 30. In this connection it is interesting to note that a second furnace which had a stack batter of 1 in 19, although using the same burden, gave no trouble due to hanging. When the furnace was blowing well the volume of blast-passed per minute was between 20,000 and 25,000 cu. ft. The average blast volume passed, however, was about 17,000 cu. ft. per minute. The blast pressure was maintained between 9 lb. and 12 lb., and the recorded blast temperature was 600°–700° C. The stock line was situated about 12 ft. down the stack, and the temperature of the outgoing gases averaged 250°–300° C. The furnace was tapped approximately every five hours and each cast contained 30–40 tons of iron. An electrical gun, operated by remote control, was used for closing the tap-hole, consequently it was unusual to take the blast off the furnace during casting. The average weekly make of iron was 1,200 tons, and during the campaign of sixty weeks 71,391 tons of iron were made. About 17 cwt. of slag were flushed for every ton of iron made. The average analysis of the slag was as follows : $SiO_2$, 32·5 per cent. ; $Al_2O_3$, 14·0 per cent. ; CaO, 48·0 per cent. ; MgO, 3·5 per cent. ; S, 1·45 per cent. ; the molecular slag ratio being 1·74.

### III. The Disposition of the Thermocouples in the Lining.

Sixteen thermocouples were inserted in the lining of the furnace prior to blowing-in. The brickwork along the horizontal joints was first chamfered off and a steel tube embedded horizontally in the brickwork. Each hole terminated originally exactly 6 in. behind the working face, the steel tube serving to align the hole throughout its length. The couples, with the exception of one bosh couple, consisted of No. 8 Chromel-Alumel wire separated by porce-

lain insulators. At the commencement the couples were not protected by any sheathing other than the steel tube lining the hole. A short steel tube extending 18 in. along the couple served to carry both the head-piece and a flange with which the tube was welded to the casing. The thermocouples were disposed in five horizontal planes, two in the bosh and three in the stack as shown in Fig. 37.

*Plane I*, 9 ft. 0 in. above the tap-hole, contained only one couple placed immediately opposite to the tap hole at the back of the furnace. This was a platinum, platinum-rhodium couple completely encased in a fireclay sheath.

*Plane II* (bosh) situated 14 ft. $10\frac{1}{2}$ in. above the tap-hole and 4 ft. 7 in. below the top of the bosh contained four base-metal thermocouples. One couple was placed directly above the tap-hole and the remaining three were orientated due north, east and
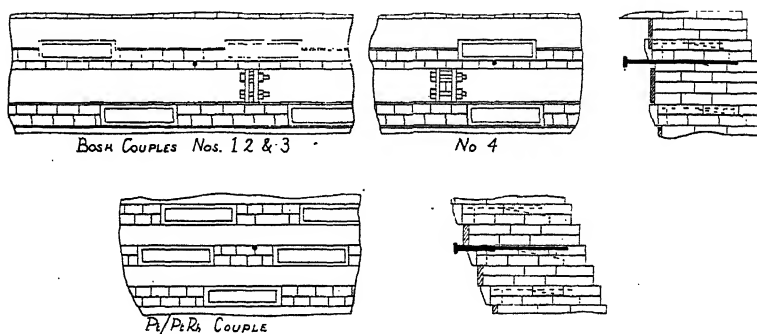


Fig 38.—Positions of the bosh couples in relation to the bosh cooling block

south respectively. For convenience the couples were numbered consecutively in a clockwise manner, No. 1 couple being over the tap-hole. Fig. 38 shows the manner in which the bosh couples were disposed in relation to the cooler blocks. No. 4 couple was placed immediately underneath a cooler, whereas all other couples were at least 6 in. from any cooler block.

*Plane III* (lower stack) was located 49 ft. 6 in. from the top of the stack, 3 ft. $3\frac{1}{2}$ in. above the top of the bosh and 6 ft. 6 in. above the lintel plate. This plane was thus 3 ft. above the topmost row of cooler blocks. Only three couples could be placed in this plane in positions 1, 2 and 4, position 3 being blocked by the hot blast main.

*Plane IV* (middle stack) was situated 35 ft. 3 in. from the top of the stack and 17 ft. $6\frac{1}{2}$ in. above the bosh. Four couples were inserted in this plane.

*Plane V* (top stack) was 19 ft. 4 in. below the top of the stack and about 5 ft. below the stock line. This plane contained four

couples arranged directly over the tap-hole and at intervals of 90° respectively.

All couples were distributed between three six-point automatic recorders housed in the room from which the automatic tap-hole gun was controlled. All leads from the couples to the recorders were accurately compensated.

IV. THE BLOWING-IN OF THE FURNACE ON DECEMBER 8TH, 1938.

For a fortnight prior to blowing-in a small fire was kept burning in the hearth. During this period the bosh and lower stack couples registered 40°–80° C. On December 8th this fire was built up with coal, wooden sleepers were inserted through the one tuyere hole remaining open, after which the last tuyere was placed in position. At this stage all the tuyeres were 3 in. in diameter.

Ten tons of coal were next charged from the bell followed by 40 tons of coke. By 4 p.m. on December 8th all the coke had been charged and this was followed by a light foundry iron burden. The method of burdening used throughout the campaign was known as four-line burdening. Each bucket of ore was followed by a bucket of coke and the bell was dropped after every bucket. The ore buckets comprised the following :—

    1st bucket : equal weights of South Wales ore, flue cinder, African ore, Oxfordshire ore.

    2nd bucket : equal weights of Swedish ore, Northampton ore, African ore, Oxfordshire ore.

    3rd bucket : equal weights of South Wales ore, Northampton ore, African ore, flue cinder.

    4th bucket : equal weights of North Staffs. ore, Northampton ore, African ore, Oxfordshire ore,

after which the cycle was repeated, the 5th bucket being identical with the first and each bucket alternating with a charge of coke.

The light burden consisted of :—

1. 12 buckets of ore at 2 tons per charge, 2 cwt. of silica rock and 2 cwt. of limestone being placed on each bucket, alternating with 12 charges of coke at 3 tons per charge plus 5 cwt. limestone.

2. 12 charges of ore at 3 tons per charge plus 2 cwt. limestone and 2 cwt. silica rock alternating with coke charges carrying 6 cwt. limestone.

3. 8 charges of ore at 4 tons per charge plus 2 cwt. limestone and 2 cwt. silica rock alternating with coke charges carrying 7 cwt. limestone.

4. The remainder of the charges were 5 tons of ore carrying 4 cwt. of limestone and silica rock, 10 cwt. of limestone being placed on each coke charge. By this means the furnace was full at noon on December 9th, and air was blown through the tuyeres at a pressure of 0·2 lb.

The blast was then increased in stages and at noon on December

TEMPERATURES IN THE BOSH AND LOWER STACK POSITIONS DURING THE BLOWING-IN PERIOD.

| Time and Date. | Hours since Blowing-in Commenced. | Temperature of Couples in the upper Bosh Plane. | | | | Temperature of Couples in lower Slack Plane. | | | Remarks. |
|---|---|---|---|---|---|---|---|---|---|
| | | 1. | 2. | 3. | 4. | 1. | 2. | 4. | |
| | | ° C. | ° C. | ° C. | ° C. | ° C. | ° C. | ° C. | |
| Dec. 8th, 8 a.m. | 0 | 100 | 90 | 80 | 70 | 75 | 90 | 55 | Small fire in hearth, all tuyeres but No. 2 in position. |
| Dec. 8th, 10 a.m. | 2 | 100 | 95 | 85 | 70 | 80 | 100 | 60 | Coal fire built up in hearth. |
| Dec. 8th, 12 noon. | 4 | 130 | 110 | 100 | 80 | 90 | 110 | 60 | Timber charged 11.50 a.m.–12.50 p.m., followed by 10 tons of coal. |
| Dec. 8th, 1 p.m. | 5 | 160 | 140 | 125 | 70 | 90 | 110 | 60 | Commenced to charge 40 tons of coke. |
| Dec. 8th, 5 p.m. | 9 | 65 | 65 | 55 | 30 | 100 | 100 | 50 | All coke charged; light burden commenced. |
| Dec. 9th, 12 noon. | 28 | 65 | 65 | 50 | 50 | 75 | 75 | 50 | Furnace full ; blast, 0·2 lb. |
| Dec. 9th, 2 p.m. | 30 | 70 | 65 | 60 | 80 | 75 | 75 | 60 | Blast increased to 0·9 lb. |
| Dec. 9th, 4 p.m. | 32 | 120 | 110 | 105 | 160 | 75 | 75 | 65 | Blast increased to 1·3 lb. |
| Dec. 9th, 6 p.m. | 34 | 185 | 150 | 180 | 230 | 80 | 80 | 75 | Blast increased to 1·7 lb. |
| Dec. 9th, 10 p.m. | 38 | 405 | 375 | 375 | 475 | 100 | 120 | 90 | Blast increased to 2·0 lb. |

| Date | 40 | 510 | 520 | 530 | 580 | 130 | 150 | 100 | Remarks |
|---|---|---|---|---|---|---|---|---|---|
| Dec. 9th, midnight. | 40 | 510 | 520 | 530 | 580 | 130 | 150 | 100 | Blast increased to 3·3 lb. |
| Dec. 10th, 6 a.m. | 46 | 775 | 760 | 780 | 790 | 265 | 275 | 180 | Blast constant at 3·4 lb. |
| Dec. 10th, 12 noon. | 52 | 870 | 895 | 895 | 780 | 400 | 425 | 345 | Blast, 3·5 lb. |
| Dec. 10th, 6 p.m. | 58 | 960 | 975 | 960 | 815 | 600 | 600 | 555 | First tap, 2 p.m.; Si, 8·05; S, 0·019; P, 0·56; Mn, 0·99. |
| Dec. 10th, midnight. | 64 | 1,010 | 1,005 | 990 | 840 | 704 | 700 | 650 | Blast, 3·1 lb. 2nd tap; Si, 5·87; S, 0·028; P, 0·53; Mn, 1·14. |
| Dec. 11th, 6 a.m. | 70 | 1,025 | 1,020 | 1,000 | 850 | 745 | 750 | 680 | Blast, 3·2 lb. 3rd tap; Si, 6·66; S, 0·019; P, 0·58; Mn, 1·22. |
| Dec. 11th, 12 noon. | 76 | 1,040 | 1,020 | 990 | 800 | 845 | 820 | 755 | Blast, 4 lb. 4th tap; Si, 5·20; S, 0·018; P, 0·54; Mn, 1·40. |
| Dec. 11th, 6 p.m. | 82 | 1,040 | 1,025 | 995 | 800 | 885 | 840 | 785 | Blast, 4·1 lb. 5th tap; Si, 5·68; S, 0·015; P, 0·49; Mn, 1·22. |
| Dec. 11th, midnight. | 88 | 1,050 | 1,020 | 1,000 | 805 | 940 | 890 | 840 | Blast, 4·3 lb. |
| Dec. 12th, 12 noon. | 100 | 1,040 | 1,010 | 1,000 | 805 | 950 | 950 | 855 | Blast, 4 lb. 6th tap; Si, 5·40; S, 0·020; P, 0·51; Mn, 1·41. |
| Dec. 12th, midnight. | 112 | 975 | 1,030 | 975 | 775 | 900 | 990 | 800 | Blast, 4·4 lb. 7th tap; Si, 5·02; S, 0·017; P, 0·50; Mn, 1·58. |
| Dec. 13th, 12 noon. | 124 | 895 | 1,055 | 955 | 730 | 875 | 970 | 775 | Blast, 4 lb. 8th tap; Si, 4·62; S, 0·020; P, 0·56; Mn, 1·37. |
| Dec. 14th, 12 noon. | 148 | 810 | 1,190 | 870 | 680 | 850 | 950 | 740 | Blast, 6 lb. 12th tap; Si, 3·05; S, 0·025; P, 0·50; Mn, 1·39; No. 2 bosh couple failed at 5 p.m. |

10th was $3\frac{1}{2}$ lb.    The first tap of iron was made at 2 p.m. on December 10th.    Table XXIX gives details of the temperatures recorded in the upper bosh and lower stack planes during the blowing-in period.    As can be seen from this table, the temperatures of the couples showed a steep rise when the blast was introduced through the tuyeres.    The rise in temperature of the bosh couples was greatest between 10 p.m. and midnight on December 9th, averaging 50°–80° C. per hour.    On the other hand the rise in temperature of the lower stack couples was more uniform.    The maximum rise in temperature of these couples occurred between noon and 6 p.m. on December 10th, when an average rise of 32° C. per hour was recorded.    During the blowing-in period it was obvious that the introduction of the blast caused the combustion of the coke at the tuyere level, which resulted in a rapid localised increase in temperature.    The rate of heating decreased with the height above the tuyeres since the hot gases passing through the cold burden became progressively cooler.    Thus the temperature of the brickwork in the stack was raised at a more uniform rate than that of the bosh lining.    Immediately in the vicinity of the tuyeres the rate of rise of temperature of the brickwork must have been excessive.    There is ample evidence from inspections made of blown-out linings that spalling occurs in the linings of blast furnaces.    It is difficult to see at what period thermal spalling could occur other than during the blowing-in.    In the lower regions of the furnace the rapid rate of heating of the brickwork at this stage provides ample cause for spalling to take place.    The blowing-in period of this furnace was very carefully controlled, and there is good reason to believe that it did not differ materially from what is recognised as general blast-furnace practice.

A second feature of the blowing-in period was the high temperatures attained in the bosh.    Nos. 1, 2 and 3 bosh couples all recorded 1,000° C. within 100 hours of commencing to blow-in.    The actual face temperature of the lining, which at this level was 2 ft. $7\frac{1}{2}$ in. thick, must therefore have been in the region of 1,200° C.    Thereafter, with the exception of couple No. 2, the remainder of the bosh couples decreased in temperature.    No. 2 couple, however, continued to increase in temperature until, 150 hours after blowing-in, 1,200° C. was recorded and the couple failed.    One likely explanation is that some brickwork had spalled away from No. 2 position, exposing the couple tip to the furnace gases.    No. 4 bosh couple read almost 200° C. below the other three couples in the same plane, which may be explained by the presence of the cooler-block situated immediately over this thermocouple.

V. THE TEMPERATURE GRADIENTS RECORDED DURING THE
  CAMPAIGN, DECEMBER 1938–JANUARY 1940.

(a) *The Working of the Furnace.*

By December 27th the 3-in. tuyeres had all been changed to
5-in. ones with the exception of the tuyere over the tap-hole, which
was kept at 3 in. for the entire campaign. During the first
fortnight of January, 1939, the furnace drove steadily, but towards
the end of the month persistent hanging of the burden occurred
and the furnace had to be pulled several times each day. By the
10th of February all the tuyeres with the exception of the 3-in.
tuyere over the tap-hole had been replaced by 6-in. tuyeres. The
furnace continued to blow at an average pressure of 10 lb. and the
weekly output of foundry iron was approximately 1,200 tons.
During February the furnace continued to give much trouble due
to hanging of the burden and it was necessary to pull the furnace
several times each day. On March 7th the furnace was changed over
to a basic burden, and destructor scrap was also incorporated.
The furnace hung so badly, however, that after a fortnight the use
of destructor scrap was discontinued. An improvement in the
working of the furnace was noticeable during the second half of
March and the beginning of April, but towards the end of April
persistent hanging again occurred and four heavy slips were experi-
enced. During May the blast pressure was increased to 12 lb. and
the furnace drove regularly until the 22nd of May, when a further
period of hanging occurred. From June onwards the furnace on
the whole drove much better. Foundry iron was made between
July 3rd–14th, August 15th–September 15th and December 26th–
28th; during the remainder of the campaign the furnace was on a
basic burden. On the 22nd July, 1939, a third blast furnace was
blown-in and this necessitated the blast being reduced from 12 lb.
to about 9 lb. Owing to the general improvement in the working
of the furnace, the production of iron was, however, well maintained
until the end of the year. The year 1940 brought grave difficulties
in connection with the smooth working of the furnace. The cold
weather caused serious transport difficulties and the supplies of
certain ores could not be maintained. The burden was continually
altered, and the furnace was only worked intermittently during
January. On January 28th the furnace was damped down, being
filled with coke followed by a light burden, the tuyeres were removed
and the tuyere holes bricked up to prevent draughting. In March
and April the furnace was raked out, the lines were measured and
the brickwork examined and patched up in July, 1940.

(b) *The Temperatures Recorded by the Couples.*

1. *The Platinum Platinum-Rhodium Couple in the Bosh.*

During January, 1939, this couple recorded temperatures
fluctuating between 400°–700°. C. On February 16th a temperature

of 900° C. was recorded and on the 20th the end of the fireclay protecting sheath probably protruded into the furnace and broke off. Momentary temperatures of 1,600° C. and over were recorded before the couple failed. On trying to remove the thermocouple, both the sheath and end of the couple were found to be firmly embedded in the lining. Potassium cyanide, metallic iron and zinc chloride were found deposited inside that portion of the sheath which could be removed. The end of the hole quickly sealed up and attempts to drill it out again were unsuccessful.

## 2. *The Bosh Couples.—Plane II*, 14 ft. 10½ in. *above the Tap-hole.*

The bosh early showed signs of erosion and during the blowing-in period No. 2 couple recorded 1,200° C. and then failed. This couple was removed and a new one inserted. On January 30th, 1939, when the furnace was hanging badly, the temperatures of this couple fluctuated violently and again recorded 1,200° C. when the couple burned out for the second time. The hole was then rammed with 5 in. of clay and a third couple inserted 11 in. back from the original face. In March, the temperatures recorded by No. 3 couple diverged from those indicated by the other couples, as may be seen from the graph (Fig. 39, Plate III), and recorded an average temperature of 900° C., with a maximum reading of 1,100° C. Until May, No. 4 couple read consistently below the other couples (with the exception of No. 2 couple now 11 in. behind the face) due to the proximity of the cooler block above. In March also the couples in Nos. 1 and 2 positions, originally reading temperatures of 800° C. and 600° C. respectively, suddenly recorded temperatures above 1,300° C., indicating that they were protruding into the furnace. Towards the end of March it was decided to replace all existing couples and to substitute new ones completely enclosed in steel sheaths. On attempting to withdraw the old couples it was found that the tips were firmly embedded in the lining. On exerting force Nos. 3 and 4 couples broke away. No trace of the tips of these couples could be found, suggesting that the 6 in. of brickwork originally in front had completely eroded away and been replaced by scar. When the sheathed couples were substituted, temperatures showed a decrease of approximately 200° C., since the surface temperature of the scar only could be measured. These scars showed evidence of continual alteration; for example, in May the temperatures of Nos. 1 and 4 couples rose considerably, indicating the removal of scars in front of these positions. This incidentally coincided with the furnace working much more regularly. On June 30th Nos. 1 and 4 couples both recorded 1,000° C. and on July 21st No. 1 couple read 1,200° C. and failed. As it was found impossible to drill new holes in the bosh region owing to the presence of cooler blocks and pipes, and as no sheaths could be withdrawn from the holes, the recording of the bosh couples was discontinued after the end of July.

### 3. *The Lower Stack Couples.- -Plane III* 49 *ft.* 6 *in. from the Top of the Stack.*

From the commencement of the campaign, gas was detected blowing out of the thermocouple holes, particularly in the middle and lower stack positions. After a few weeks Nos. 1 and 2 couples slowly recorded a decrease in temperature, after which they continued to read without any marked variation. It was soon found that these couples had been attacked by the blast-furnace gas and they had to be periodically replaced by new couples. The sheathing of all couples at the end of March, however, greatly prolonged their useful life. During January and February the temperatures in the lower stack were comparable with those in the middle stack. In March the temperatures increased, No. 2 couple recorded 1,000° C. and No. 4 couple 920° C. In common with all the stack couples the temperatures recorded by those in the lower stack dropped during April and increased again in May. Early in May, No. 4 couple failed after recording 900° C., presumably due to the end of the sheath burning away. During the month of June temperatures were again high in the lower stack region, No. 2 couple recording 1,100° C. When couples failed they could not be withdrawn from the holes, so that provision had to be made to drill fresh holes into the lining. By July all the old couples had been abandoned and new couples were inserted in holes drilled out to a depth of 12 in. into the lining. During the drilling it was found that the brickwork in No. 4 position was softer than in the other positions. Samples of the drillings from Nos. 4 and 1 positions were found, however, to contain only 0·43 per cent. and 0·26 per cent. of carbon respectively. In November No. 4 couple failed, probably due to penetration of gas through the porous brickwork. During the latter period of 1939 temperatures for the lower stack positions were slightly lower than for the corresponding positions in the middle stack. Peak temperatures of 600° C. were recorded by No. 1 couple in the latter part of November and by No. 2 couple in January, 1940, although these couples were 2 ft. 9 in. behind the original face.

### 4. *The Middle Stack Couples.—Plane IV,* 35 *ft.* 3 *in. below the Top of the Stack.*

As with the lower stack couples, the middle stack couples suffered seriously from attack by gas and had to be checked frequently and occasionally replaced. When the furnace production was changed to basic iron all temperatures increased and, towards the middle of March, 900° C. was recorded. All couples were renewed and sheathed early in April and the holes examined. There was evidence of erosion of the lining in No. 4 position and the new couple was withdrawn to a distance of 21 in. behind the original face. On removal prior to sheathing, No. 2 couple had a

heavy incrustation of ammonium chloride both in the hole and the head-piece of the couple. Beads of metallic lead had deposited on the insulation of No. 3 couple and zinc chloride was found, together with iron and aluminium chlorides. The presence of these two latter salts might, however, be attributed to corrosion of the thermocouple wires and sheaths.

During May temperatures again increased and the couples and sheaths were firmly fixed in the holes. By the end of May new holes were cut into the brickwork to a distance of 12 in. and new couples inserted. Samples of the drillings from No. 2 position were found to contain 0·65 per cent. of carbon. All couples registered high temperatures towards the middle of July, No. 1 couple reaching 630° C. Peak temperatures recorded were as follows : No. 1 couple, 800° C. (November 21st) ; No. 2 couple, 680° C. (January 6th, 1940) ; No. 3 couple, 720° C. (November 11th) ; and No. 4 couple, 700° C. (October 23rd). The temperatures of these couples are shown in Fig. 39.

5. *The Top-stack Couples.—Plane V, 19 ft. 4 in. from the Top of the Stack.*

In the top stack all four couples read approximately the same temperature at any period and fluctuated in a similar manner. During February, 1939, the average temperature of all couples was 660° C., which rose to 700° C. on changing the tuyeres from 5 in. to 6 in. In common with the other couples the top stack couples were renewed and completely encased in steel tubes during April, although there appeared no tendency for the exposed couples in this plane to be attacked to the same extent by blast-furnace gas. Tarry matter had, however, been deposited on the couples, although sound brickwork was present at the end of all holes. During May and June temperatures showed an increase, and at the end of the month Nos. 2 and 3 couples read 880° C. and 860° C. respectively. Towards the end of July Nos. 1 and 2 couples recorded temperatures of 900° C. and a week or so later No. 2 couple failed. By the end of August temperatures had dropped to 600° C. All couples and sheaths were removed from the holes in September, 1939, the existing holes were shortened to 12 in. in length by ramming with clay and new couples were inserted this distance into the lining. From mid October until the damping down of the furnace temperatures in the top stack remained fairly uniform, as may be seen from Fig. 39.

VI. Deductions Drawn from the Records of Temperature Gradients.

(a) *Temperatures in the Bosh.*

There was general agreement between the temperatures recorded by the couples in all three stack planes. These tempera-
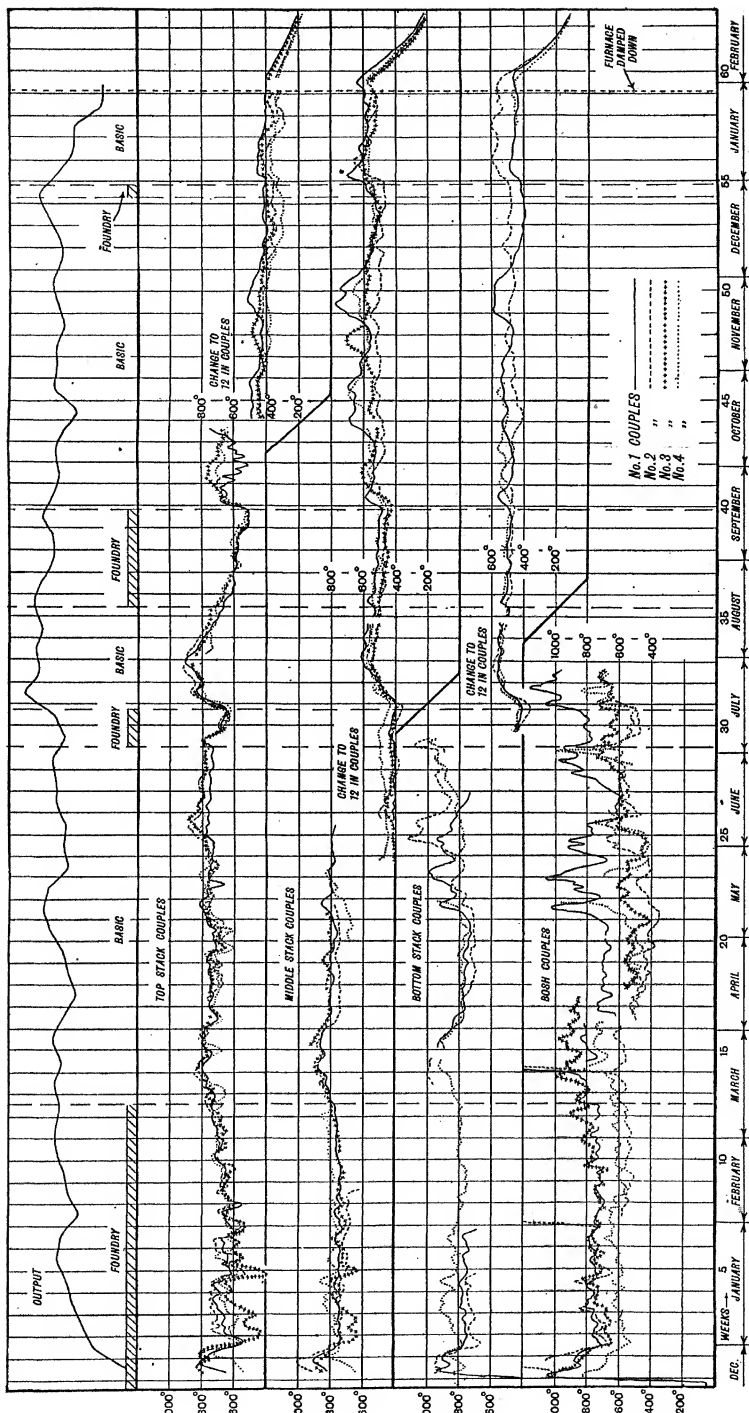
PLATE III.

Fig. 39.—Records of the temperatures of couples in the bosh and stack planes during the campaign.

[To face p. 144.

tures, however, bore no relation to those obtained in the bosh. The bosh couples showed daily fluctuations over a temperature range of about 100° C. and these variations occurred independently with each couple. It would appear that the temperatures in the bosh lining were primarily dependent on the accumulation and subsequent removal of scars on the working face. The records indicated that the slow building up of temporary scars, followed at a later stage by their sudden and complete removal, were general features of the bosh region. It appeared probable that the falling away of these temporary scars was also attended by the disappearance of some of the actual brickwork which might have slagged with the scar. The bosh temperatures were probably also influenced by localised burden slips.

(b) *Temperatures in the Stack.*

1. *The Temperatures at the Lining Face.*

It has been estimated from the temperatures recorded 6 in. behind the working face that when the furnace was on a basic burden average inwall temperatures were as follows : top stack plane, 19 ft. 4 in. down the stack, 905° C. ; middle stack plane, 35 ft. 3 in. down the stack, 1,010° C. ; bottom stack plane, 49 ft. 7 in. down the stack, 1,035° C. These temperatures are considerably higher than those generally accepted for the middle and upper regions of blast-furnace stacks. In a previous paper [1] the authors contrasted inwall temperatures of various furnaces and showed that great diversity existed dependent on whether the gases tended to pass through the centre of the burden or through the peripheral layers. The flow of gases in turn was controlled by the segregation of the burden. A further note on the segregation of the burden and its effect on blast-furnace linings is included in an appendix. In this particular furnace it appeared that there was a tendency for the burden to segregate, the large pieces of ore and probably the majority of the coke falling towards the lining wall. The increased porosity of the periphery of the burden was thus responsible for a rapid flow of gas at the lining face. As has been demonstrated by S. P. Kinney [3] a high gas velocity is in turn indicative of both high temperatures and maximum percentages of carbon monoxide in the gas. The conditions which obtained in this furnace were therefore severe on the lining, the high inwall temperatures favouring slagging, alkali attack and penetration of volatile salts, whereas the high carbon monoxide content of gas in contact with the lining would tend to give optimum conditions for carbon monoxide disintegration behind the working face. There can be but little doubt that the centre of the stock must have been very much cooler than the periphery, since the top gas temperature was only 250°–300° C., although the inwall temperature 5 ft. below the stock line was 900° C.

## 2. *Correlation of the Temperatures of the Stack Couples.*

● There was general correlation between the temperatures recorded by all couples in the stack. Two distinct types of variations could be distinguished. First, those variations which were recorded by all stack couples simultaneously and, secondly, variations which only affected the couples on one particular side of the furnace. Generally, at all positions in the three planes, temperatures tended to rise and fall during the same periods. These variations were most marked with the couples in the middle stack positions and least marked with those in the top stack. The temperature variations, as may be seen from Fig. 39, occurred in cycles, and took the form of a steep rise extending over a period of four to ten days, followed by a more gradual fall. The average trend was, however, for the temperatures in the middle and lower stack positions to show a gradual overall increase in temperature which could only be ascribed to the continuous wearing back of the lining face. The short periods of increasing temperature commenced on March 7th, July 17th, September 18th, October 12th, 1939, and January 1st, 1940. These temperature rises coincided with alterations of the burden from foundry iron to basic iron which took place on March 7th, July 15th, September 15th, and December 29th. The reverse changes from basic to foundry iron did not produce similar rises in temperature. Further, when the furnace was making foundry iron, temperatures were low and uniform over each plane. When producing basic iron, temperatures were generally higher and there were often considerable deviations between the readings of the couples in any one plane. The foundry burden had a slightly higher coke to ore ratio than the basic burden ; in addition the basic burden included an increased percentage of Northamptonshire ores and basic slag, substituted in part for the African ore and flue cinder of the foundry burden. The net result, however, was that the foundry iron burden contained rather less fines and was consequently more porous to the gases than the basic burden. On the whole the furnace drove better when making foundry iron. It would be expected that the foundry iron burden, containing less fines, would tend to give more even distribution of the gases in the stack, while the basic burden would tend to increase the proportion of gas passing through the peripheral layers in relation to that passing through the centre of the stock. This offers an adequate explanation for the rise in temperatures at the inwall when basic iron was made, since the increased content of fines in the basic burden was largely concentrated at the centre of the stock column. The increase in temperatures noted in October has not been satisfactorily explained, but in this connection it is interesting to note that a second furnace burdened in exactly the same manner recorded a corresponding rise in inwall temperatures over the same period.

An increase in temperature occurring up one side of the furnace only was regarded as evidence of the channelling of gases in the

burden.    In May there was evidence of such channelling up No. 7 side of the furnace, and in November up No. 1 side.    This preferential channelling up one particular side of the furnace probably resulted in rapid localised erosion of the lining.    The significance of these observations was clearly established when the blown-out furnace was inspected and maximum wear was found to have occurred between Nos. 1 and 4 positions.

## VII. THE DAMPING-DOWN OF THE FURNACE.

During January, 1940, the furnace was worked intermittently. The longest period when the blast was off was 36 hours.    During the intermittent working periods the temperatures of all couples remained fairly constant and showed no tendency to rise and fall with the turning on and off of the blast.    On January 28th, 1940, the furnace was damped down by feeding 35 charges of coke blanks followed by a light burden.    Temperatures recorded 12 in. in the lining did not commence to drop until the blast had been shut off for at least 48 hours.    In all three planes the rate of cooling was slow and uniform, being $9\frac{1}{2}°$ C. per day in the top stack and 18°–20° C. per day in the middle and lower stacks.    These figures do not, of course, represent the rate of cooling of the face but of positions 12 in. inside the lining.    It would be expected that at such positions considerable delay would ensue before any temperature changes at the working face were communicated to the couples.

## VIII. ESTIMATED THICKNESS OF THE LINING FROM TEMPERATURE DATA.

The principal object of this investigation was to record temperatures with a view to detecting the wearing back of the lining. The method used in calculating the thickness of the lining depends on the assumptions of a linear temperature gradient through the brickwork and an outer wall temperature of 100° C.    It was also taken as a reasonable basis for calculation that, after 15 weeks (when the 6 in. tuyeres were in position), the furnace was working normally.    At this time the average temperatures of the top, middle and bottom stack couples were 785°, 890° and 910° C. from which it may be deduced that the face temperatures of the lining under average conditions were about 905°, 1,010° and 1,035° C. in the top, middle and bottom of the stack respectively.    Using these face temperatures and the recorded temperatures of the couples at the end of June, 1939, and immediately prior to damping down, the thickness of the brickwork in the various positions was calculated.    The results are given in Table XXX, where they are compared with the measured thicknesses before and after the campaign.

On the whole the calculated thicknesses of lining (column 3) compare well with the actual thicknesses given in column 5.

TABLE XXX.—ESTIMATED AND ACTUAL THICKNESS OF LINING.

| Position of Couple. | Estimated Thickness of Lining in Inches. | | Actual Thickness of Lining in Inches. | |
|---|---|---|---|---|
| | June 30th, 1939. | Jan. 27th, 1940. | Dec. 8th, 1938. | After Blowing Out. |
| Top stack 1 | 43 | 31 | | 37 |
| ,,      2 | 40¾ | 40 | 40½ | 38½ |
| ,,      3 | 40¾ | 34½ | | 40½ |
| ,..      4 | 40¾ | 40 | | 40½ |
| Middle stack 1 | 36½ | 22¾ | | 25½ |
| ,,      2 | 39 | 24¾ | 40½ | 27 |
| ,;      3 | 34 | 25½ | | 32½ |
| ,,      4 | 28¾ | 23¼ | | 34 |
| Bottom stack 1 | | 32 | | 30 |
| ,,      2 | 44½ | 23¼ | 45 | 20½ |
| ,,      4 | 45½ | 31 | | 31¼ |

Exact agreement cannot be expected as the calculations depend on assumptions which cannot easily be verified.   The calculated wear in the middle stack region was, however, in excess of the actual wear.   This can readily be explained as the thermocouples were located in joints in the brickwork, and, on examining the working face, it was noticed that the joints had worn back for a distance of several inches behind the actual face as measured from the nose of the bricks.   At the end of June, 1939, the estimated lines of the furnace revealed that considerable channelling had taken place up the No. 1 to 4 side of the furnace in the middle stack position. This channelling probably occurred in May and early June when temperatures in the whole stack region were high.   The actual blowing-out lines of the furnace are given in Fig. 40.

EXAMINATION OF THE BLOWN-OUT FURNACE, JULY, 1940.

In July, 1940, a platform was placed in the empty furnace and the lining was examined in situ.   In the bosh and lower stack region were heavy scars several inches thick which adhered firmly to the face.   It is significant that these scars were only present in that portion of the furnace which was water-cooled.   Between the bottom and middle stack positions there appeared to be fairly even wear all round the furnace.   The joints had penetrated back into the lining and in places the bricks had rounded noses.   In No. 4 position the brickwork was smooth and hard.   From the middle to the top stack position the brickwork had worn back to a depth of 13½ in. between Nos. 1 and 4 positions and the lining was scoured to form a vertical channel which terminated quite sharply towards

the top.  Above this channel the brickwork was in very good condition, the face being hard and smooth.  The armouring in the throat appeared also to be quite unaffected.  There were, however, several open vertical cracks extending for a considerable distance
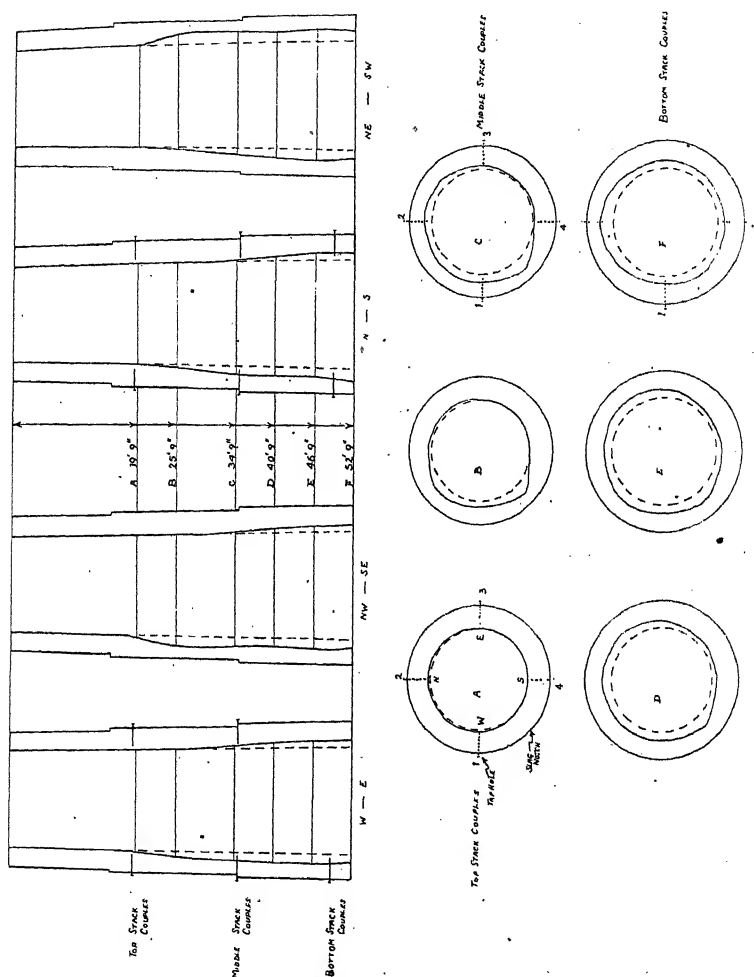


Fig. 40.—The blowing-out lines of the furnace.

through the lining due to some subsidence of the brickwork as a whole, probably during the blowing-in of the furnace.  It is interesting to note that in previous campaigns the lining of this furnace has shown a similar type of wear between tap-hole and slag notch.  The small tuyere over the tap-hole would undoubtedly tend

to deflect the gases in such a way that they swept up the face of the lining in No. 1 position. Tuyeres which do not all take the same wind must tend to make for an uneven gas distribution at the outset.



Fig. 41.—Brickwork attacked by alkali, showing crystals of kaliophilite in the surface of the slag in zone I (crossed nicols × 80).
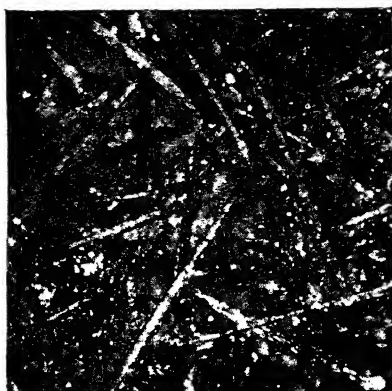


Fig. 42.—Crystals of leucite and mullite between zone I and the brick-slag interface. (Crossed nicols × 80.)

The only repair necessary was a patch of new brickwork which was corbelled into the lining at the top of the channel 20 ft. down the stack. Old brickwork removed from this position was found to be blue-grey in colour, there were no obvious carbon spots, but the surface of some of the bricks had been slagged to a depth of about

one-quarter of an inch.· This slag, when chipped away from the brick, had the following percentage analysis : $SiO_2$, 53·59 ; $TiO_2$, 1·23 ; $Fe_2O_3$, 3·00 ; $Al_2O_3$, 30·89 ; CaO, 2·24 ; MgO, 1·83 ; $K_2O$, 3·78 ; $Na_2O$, 1·53 ; $SO_3$, 0·35 ; and loss on-ignition, 0·24. A micro-section cut through the slagged area revealed (1) a surface zone comprising a thin deposit of carbon followed by crystallisation of $\beta$ kaliophilite or possibly a solid solution of kaliophilite, $K_2O$.
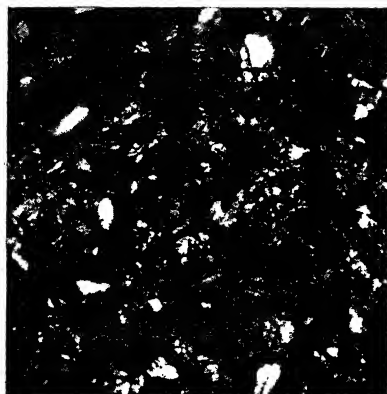


Fig. 43.—Quartz crystals changing to tridymite at the brick-slag interface.
(Crossed nicols × 80.)

$Al_2O_3.2SiO_2$, and $\beta$ nephelite, $Na_2O.Al_2O_3.2SiO_2$ (Fig. 41) ; (2) an intermediate zone containing leucite, $K_2O.Al_2O_3.4SiO_2$, and mullite, $3Al_2O_3.2SiO_2$ (Fig. 42) ; (3) a zone at the surface of the brick proper containing deposited carbon and isolated patches of quartz partially converted to tridymite (Fig. 43). The presence of tridymite at the slag-brick interface is additional confirmation that the brickwork in this position was exposed to temperatures above 875° C., which is the conversion temperature of quartz to tridymite.

CONCLUSIONS.

·The insertion of thermocouples in the stack and bosh brickwork of a blast furnace has indicated the rate at which the lining wore back during a campaign of fourteen months. On the bosh the formation of temporary scars was suggested by the rapid fluctuations in temperature shown by the couples. The temperature records have also revealed any tendency for the gases to channel at any time up one particular side of the furnace stack. Valuable inferences have also been drawn relating to the segregation of the burden in the stack and the driving of the furnace generally. It is considered possible from the temperature records to compute with

reasonable accuracy the thickness of the lining in front of any thermocouple and thereby to obtain an estimate of the lines of the furnace at any particular time during the campaign.


# APPENDIX.

## A FURTHER NOTE ON THE SEGREGATION OF THE BURDEN IN BLAST-FURNACE STACKS.

There would appear to be general agreement that the segregation of the burden determines to some extent the temperature isothermals existing in the stack, thereby influencing the temperature of the lining face and the gradient through the lining. S. P. Kinney [3] and co-workers have pointed out from a study of American furnaces that high velocities of gas, high temperatures, and maximum carbon monoxide content of the gas exist together in the furnace stack. The valuable researches carried out by the Blast Furnace Reactions Research Sub-Committee of the Iron and Steel Federation have previously thrown considerable light on the effect of segregation of the burden. The present authors have quoted these researches when drawing attention to the marked differences in temperature gradients which can exist in various blast-furnace linings. It is now proposed from the viewpoint of segregation of the burden, that blast furnaces might be classified into three main types.

*Type* (1), where the temperature in a horizontal plane in the stack continually increases from the inwall to the centre of the burden. This type of furnace has been discussed by the authors in a previous report [4] where it is referred to as furnace A. The temperature gradient across the stack was in the form of a pyramid $\bigwedge$, the stock being more porous at the centre of the column where temperatures and gas velocities were high. The change was progressive to the inwall where the stock was composed of smaller particles and the gas velocity was low.

*Type* (2). This is the reverse of type (1) and perhaps does not exist as an extreme case. Here the temperatures in the stack are a maximum at the inwall and continually decrease towards the centre of the burden. The temperature gradient would take the form of a $\bigvee$, but in actual practice it is probable that the base of the $\bigvee$ is considerably flattened. Examples of furnaces approximating to this case are one described by Kinney, [5] possibly the furnace investigated by H. W. Johnson, [6] and the furnace which has formed the subject of this investigation.

*Type* (3). This may be considered intermediate between types 1 and 2 and is well exemplified by the Frodingham furnace forming the basis of Report No. 1 of the Blast Furnace Reactions

Research Sub-Committee.[7]   The temperature gradients in a horizontal plane through the stack took the form of a $\vee\!\vee$, maximum temperatures occurring both at the inwall and the centre of the stock column.   If the central apex becomes less pronounced ($\vee\!\vee$) furnaces of this would approach type (2), and vice versa; with a more pronounced central apex such furnaces would approach type (1) ($\wedge\!\wedge$).

It is feasible to assume that these zones of varying temperature are due to segregation of the burden as it drops into the furnace. The burden is more porous in the high temperature zones and, accordingly, the gas in these zones has a higher velocity.   In Report No. 1 relating to the Frodingham furnace the stock line contour is drawn and is in the form of a letter $\wedge\!\wedge$, the larger pieces of the burden rolling into the troughs and the fine particles falling vertically from the bell and occupying the heights of the stock line.   If it is a general rule that the troughs in the stock line locate the zones of high porosity in the burden, then the type of stock lines for furnaces of type (1) would be $\vee$ and for furnaces of type (2) $\wedge$.

The suggestions may be briefly summarised as follows :—

(1) The temperature conditions of the stack and lining are determined principally by the segregation of the burden.

(2) The segregation of the burden is probably related to the contour assumed by the stock line.

(3) Among the factors on which segregation of the burden depends are probably the following :—

(a) The variation in the size of ore, coke and stone.

(b) The method of distributing the charge on the large bell.

(c) The bell clearance and bell angle.

(d) The distance of the stock line below the bell.

(e) The time required to open the large bell.

(f) The distance through which the bell is dropped between open and shut positions.

(g) The presence of lugs and other irregularities on the surface of the bell.

It would appear from our observations, coupled with those reported by the Blast Furnace Reactions Research Sub-Committee, that furnaces of type (1) are favoured by (a) a small bell clearance, and (b) a high stock line, and furnaces of type (2) by (a) a large bell clearance and (b) a low stock line.

REFERENCES.

1.  G. R. Rigby and A. T. Green, *Bull, B.R.R.A.*, **55,** 39, 1940.
2.  J. Stoecker and A. Rein, *Stahl Eisen,* **58,** 965, 1938.
3.  S. P. Kinney, P. H. Royster and T. L. Joseph, *Bur. of Mines, Tech. Paper,*
        No. 391, 1927.
4.  G. R. Rigby and A. T. Green, *Bull. B.R.R.A.*, **55,** 40, 1940.
5.  S. P. Kinney, *Blast Furnace and Steel Plant,* **152,** 209, 1934.
6.  H. W. Johnson, *ibid.*, **165,** 590, 689, 1938.
7.  *Iron and Steel Inst., Special Report No.* 18, 1937.

# Section D.

## (6) Summary of other Published Work of the British Refractories Research Association of Interest to the Iron and Steel Industry.

BASIC REFRACTORIES.

In addition to the papers on basic refractories reprinted in the present Report, the B.R.R.A. has published some twenty other papers on the subject since the First Report was issued. A comprehensive review of the sources, methods of manufacture, and properties of basic refractory materials was prepared in 1940; this review consisted of some two hundred pages and was arranged to afford easy reference to the world's literature on the subject.

Experiments have indicated [1] that dolomite may be stablised by the calcination of a mix comprising 85 per cent. of raw dolomite, 6 per cent. of silica sand, and 9 per cent. of ferric oxide. Dolomite bricks of fairly satisfactory properties have been produced from the clinker, although their spalling resistance was rather low. Composite bricks prepared from dolomite clinker stabilised in this manner and Rhodesian chrome ore showed improved properties compared with bricks prepared from either component. It was found advantageous, particularly from the standpoint of thermal spalling, to include a proportion of the dolomite clinker in the intermediate size fraction. Calcination of a mixture of Shetlands chrome ore and raw dolomite in proportions to give, after firing, 75 per cent. of chrome ore and 25 per cent. of calcined dolomite, resulted in a clinker from which bricks were produced which proved satisfactory in laboratory tests.

Bricks have also been prepared [2] from synthetic merwinite, $Ca_3Mg(SiO_4)_2$, using silica sand, lime and dolomite as raw materials and 1 per cent. of boric oxide as mineraliser. In laboratory tests the product was found to have a low refractoriness-under-load and poor resistance to basic slag and thermal shock.

It has been found [3] that by incorporating with raw dolomite sufficient silica to convert the lime to calcium orthosilicate, together with a suitable stabilising agent, it is possible to produce a dolomite material of high porosity (60–70 per cent.) ; bricks so formed had a high refractoriness and adequate mechanical strength. The thermal conductivity of the fired material was found to be very low, comparing favourably with that of other high-temperature insulating products. Further work [4] on this type of material has shown it to have a high refractoriness-under-load, but low resistance to thermal shock. The addition of 25 per cent. of precalcined material to the raw batch had only a slightly adverse effect on the thermal

11                                          155

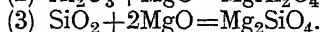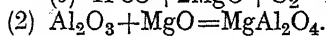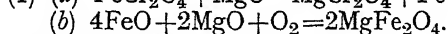conductivity, porosity and bulk density, and increased the mechanical strength.

The use of dolomite as a basis for the extraction of magnesia from sea-water is now well known ; other methods for the economic production of magnesia from dolomite have been suggested. Methods investigated [5] by the B.R.R.A. have depended on the interaction of dolomite with silica to form calcium orthosilicate and free periclase ; on cooling, the clinker fell to a powder owing to the inversion of the orthosilicate. Differences in grain size, specific gravity and electrostatic properties of the periclase and calcium orthosilicate have been used in attempts to separate the magnesia, but with only limited success.

Alternative to the removal of the lime is its stabilisation. This is a normal method of production of refractories from dolomite and other calcareous materials. Stabilisation with silica, however, is liable to lead to the formation of calcium orthosilicate, which, unless it is itself stabilised, will " dust " on cooling. Experiments have been carried out [6] which have indicated that the disintegration can be prevented by the addition of boric or phosphoric oxide ; the presence of as little as 0·05 per cent. of $P_2O_5$ appeared to be effective. The mechanism of the stabilisation is apparently not due to increased glass formation. The converse change of the low-temperature modification of calcium orthosilicate into a high-temperature form was shown to be sluggish.

As part of a study of the slagging of dolomite refractories, the fusion relations of mixtures of magnesite, stabilised dolomite, and basic slag, have been examined.[7] A continuous increase in the fusion temperature was observed with increasing base content. The fusion relations of mixtures of calcined dolomite, silica and basic slag have also been determined. The addition of silica to dolomite was found to lower the fusion points of mixtures with a constant slag content in a progressive manner. With silica additions up to that necessary to convert the lime of the dolomite into the orthosilicate, the isotherms approximated to straight lines across the ternary diagram ; no abrupt change in the fusion relations was observed as the tricalcium silicate composition was traversed. Whereas the solubility at 1650° C. of unstabilized dolomite in basic slag appeared to be comparable with that of magnesite, the solubility of dolomite-silica clinkers in the slag was found to increase with the silica content.

Work on chrome-magnesite refractories has included an investigation of reactions between mixtures of chrome, magnesia and alumina. As a preliminary the influence of boric acid and of calcium fluoride in promoting reaction was studied. [8] The influence of the two mineralisers was found to depend on the composition of the batches. Measurements of change of colour and density and examination under the microscope of mixtures of synthetic chromite with pure magnesia and alumina indicated that chrome spinel can

take a considerable amount (at least 30 per cent.) of alumina into solid solution. Free magnesia was found to occur over a wider range of composition in mixtures of chrome ore, dead-burned magnesite and alumina, than in the mixtures of pure oxides. It is probable that the reduced proportion of actual chromite present in the former series, limits the amount of magnesia which can be taken up. The microscope revealed that batches with a 30 per cent. addition of alumina become homogeneous on firing, the product having the properties of a spinel. With 50 per cent. of alumina added, free alumina was observed. In continuation of this study,[9] the constitution of the fired mixes was examined by a chemical method, in which the free periclase was extracted. The results obtained confirm that the following reactions probably take place :

(1) (a) $FeCr_2O_4 + MgO = MgCr_2O_4 + FeO$.
  (b) $4FeO + 2MgO + O_2 = 2MgFe_2O_4$.
(2) $Al_2O_3 + MgO = MgAl_2O_4$.
(3) $SiO_2 + 2MgO = Mg_2SiO_4$.

Reaction (3) occurs only when siliceous impurities are present, e.g., serpentine in the chrome ore. Continued reaction between the constituents of chrome-magnesite products during firing and subsequent use may lead to the formation of liquid. Calculation of the mineralogical constitution of a series of chrome-magnesite bricks has shown [10] that at room temperature the proportion of eutectic present under equilibrium conditions would vary only from 2 to 7 per cent. ; at 1,500° C., however, the liquid content would vary from 4 to 15 per cent. Correlation of the calculated amount of liquid formed with the refractoriness-under-load values, indicated that if the liquid content at high temperatures is too low (less than about 5 per cent.) the brick will shear under load, whereas if too much liquid is present (more than about 10 per cent.) considerable subsidence may be expected. Evidently the quantity of liquid found in chrome-magnesite bricks at high temperatures is critical, and the mineralogical constitution of these products is of considerable industrial importance.

The abnormal firing expansion, high porosity and friability of certain chrome-magnesite bricks have been attributed [11] to the use of chrome ores which show abnormal expansion in a reducing atmosphere ; the effect may occur at temperatures as low as 450° C. Chrome-magnesite bricks made from certain of these ores show the effect if heated for a sufficiently long period in reducing atmospheres, or if exposed during use in steel furnaces to iron oxide from the furnace bath. It has been found that the ores which show the most marked growth in a reducing atmosphere are generally more ferruginous than the unaffected ores.

Related to the work on chrome-magnesite refractories are some preliminary investigations [12] of chrome-lime mixtures. Finely ground mixtures of 85–70 per cent. of chrome ore and 15–30 per cent.

of limestone were fired for $1\frac{1}{2}$ hours at 1,650° C.   The fired clinkers were crushed, graded and made into test-pieces which were fired at 1,550° C. for 2 hours.   The temperature of initial subsidence under load of the mix originally containing 30 per cent. of limestone was 1,490° C., compared with 1,350° C. for the chrome ore itself ; final failure occurred at 1,650°· C. and 1,370° C., respectively.   The tendency of the chrome-lime products to hydrate was low.   A slight improvement in resistance to spalling was observed with the mixtures containing 15 and 20 per cent. of limestone.   Sillimanite-chrome mixtures have also received attention.[13]   A marked increase in the resistance of sillimanite to ferruginous slags was effected by the incorporation of moderate amounts of chromic oxide, without seriously detracting from other properties of the material.   Resistance to thermal shock was unaffected and the refractoriness-under-load was only slightly lowered by the addition of up to 13 per cent. of $Cr_2O_3$ to the sillimanite ; further additions led to appreciable reduction in the temperature of initial deformation without any marked compensation in increased slag resistance. The incorporation of chrome ore in place of chromic oxide gave less satisfactory results.   The resistance to thermal shock was unchanged, while the temperature of initial deformation under load was reduced ; the improvement in slag resistance was also less pronounced.

Work on magnesite refractories has included [14] an attempt to correlate their texture and refractoriness-under-load characteristics. The texture was evaluated by impregnation of a polished surface with a white pigment, followed by a photographic and photometric technique.   The most satisfactory products were characterised by uniformity in their pore system.

Research of a fundamental character related to basic refractories has dealt with the synthesis and study of many of the minerals likely to occur in such products.   The first paper [15] on this subject dealt with the binary silicates of lime and magnesia and the following ternary compounds : Akermanite, diopside, monticellite, merwinite, cordierite, gehlenite and anorthite.   An important finding was that anorthite shows a reversible inflexion at about 800° C., which results in a marked increase in the coefficient of expansion over the temperature range 750–900° C.    The small irregularity noted in the thermal expansion curves of firebricks in the region of 800° C. can be satisfactorily attributed to the presence of a small, percentage of anorthite.   Finally, the thermal expansions of various dolomite products were studied, including both a used and an unused brick and a sample taken from a dolomite hearth.   An unexplained permanent expansion between 925° C. and 1,200° C. was found to occur in the dolomite materials after various heat treatments. After the used brick had been tested to 1,200° C. a permanent growth of 0·74 per cent. linear was observed.   On repeating the expansion test at 1,200° C. with the same test-piece, there was a

further growth of 0·56 per cent. linear ; a third reheating resulted in a growth of 0·25 per cent.   Thus, after having been fired three times to 1,200° C., the used dolomite brick had grown 1·55 per cent. Since no similar effect was found on heating tricalcium silicate, the possibility of growth due to dissociation of this mineral was ruled out.

Later work [16] on the thermal expansion characteristics of minerals likely to occur in basic refractories has dealt with the four calcium aluminates, the two calcium ferrites, ferric oxide and brownmillerite.   It was found that the percentage reversible expansion of the aluminates decreases as the alumina content increases.   The mineral $3CaO.5Al_2O_3$ has an exceptionally low coefficient of expansion, particularly at temperatures up to 500° C. The thermal expansions of the ferrites were found to be high, of the same order as that of ferric oxide itself.   In view of the low coefficient of expansion and comparatively high melting point of the mineral $3CaO.5Al_2O_3$ (1,735° C.) it was thought that some interest might attach to a product in which the lime of the dolomite was in combination as this aluminate.   Accordingly sufficient alumina was added to a dolomite to convert all the magnesia to spinel and all the lime to $3CaO.5Al_2O_3$.   The mix was twice fired to 1,530° C. ;   during the second firing the specimens suffered little shrinkage and the final product was hard and dense.   The thermal expansion of the product was intermediate between those of spinel and of $3CaO.5Al_2O_3$, considerably below that of a commercial dolomite product.   The refractoriness of the material was found to be cone 29.

The work on synthetic minerals so far described is concerned chiefly with dolomite and magnesite refractories.   Studies have also been made [17] of some of the spinels likely to occur in materials containing chrome ore.   The minerals investigated were chromite magnesium aluminate, picrochromite, hercynite, magnesioferrite and magnetite.   It was found that the expansion characteristics of each spinel were intermediate between those of its constituent oxides.   This investigation is being continued.

THE ACTION OF SLAGS, VAPOURS AND GASES ON REFRACTORY MATERIALS.

Parts 1 and 2 of a study on the general mechanism of the action of slags on refractory materials were included in the First Report ; Part 3 has dealt [18] with the action of a series of lime/alumina/silica/ iron-oxide slags on an aluminous firebrick.   In the earlier work it was shown that anorthite is the chief product of reaction between fireclay products and lime-alumina-silica slags.   The later studies have shown that " iron "-free anorthite can also crystallise out from the interaction of firebrick and slags containing in addition notable amounts of iron oxide.   It was found that the lowest-melting composition occurs approximately at the apex of the

anorthite field in the quaternary system ; the composition of this point is probably not far removed from the quaternary eutectic between anorthite, magnetite and mullite.

The action of iron oxide on electrically fused alumina and magnesium aluminate has received attention as a corollary to the study of the isomorphous growth of chrome spinel when exposed to iron oxide. Preliminary experiments [19] were concerned with the production of suitable test materials, and the selection of satisfactory mineralisers to promote intercrystallisation. Boric acid and calcium fluoride added to the extent of 2 per cent. were found to be the most effective, and were used in the subsequent experiments. The alumina products were hard and compact, but the synthetic spinel products were comparatively weak, owing to a considerable firing expansion. The action of hammer-scale on both the alumina and spinel products was found in general to be disruptive ; the tendency was less marked in the materials mineralised with calcium fluoride than in those to which boric oxide had been added. It appeared that the effect of the hammer-scale on these products was of a similar nature to that on chrome materials. The action of basic open-hearth slag was not so vigorous.

As an aid in the study of slag attack and the effects of prolonged heating on refractory materials, a technique has been developed [20] for determining the amount and composition of the liquid formed under such conditions. The method consists in heating the test-pieces, in the form of a compressed cylinder placed on platinum foil, at the prescribed temperature until equilibrium is attained. The test-cylinder is then placed on a larger cylinder prepared from a pure refractory oxide, and the assemblage is heated at the required temperature. Any liquid formed will tend to drain into the pure oxide base, and can be analysed. Some preliminary work has been carried out, using this technique, for studies on chrome-magnesite refractories. Observations have also been made [21] on the draining of slags at high temperatures. A basic open-hearth slag on heating very rapidly to 1,350° C. was found to be completely fluid, whereas on heating slowly no signs of fusion appeared even at 1,650° C. Visual observations suggested that there had been drainage of some constituent from the slag during the slow heating, leaving a skeleton of increased refractoriness. This was confirmed by heating slag pills of known weight to various temperatures, cooling, and noting the loss in weight ; the extent of drainage was found to depend mainly on the firing temperature. A basic electric oxidising slag, an acid open-hearth slag, and synthetic slags were found to behave similarly. Analyses of the basic open-hearth slag after heating to different temperatures showed that marked changes in composition had occurred. Calculations based on the amount of drainage, and the analyses of the residual slags, indicate that at 1,450° C. compounds approximating to $2CaO,R_2O_3$ drain away, while between 1,550° C. and 1,650° C. the

drainage liquid consists mainly of calcium phosphates, silicates and/or silico-phosphates. After having been fired to 1,650° C., the residual slag appeared to consist of a mixture of calcium orthosilicate and calcium phosphates. The significance of these observations relative to laboratory slagging tests and the production and use of refractories has been briefly discussed.

It has long been appreciated that eutectic formation plays an important part in the slagging of refractories. A few of the ternary eutectics which occur in mixtures of lime, alumina, silica and magnesia have been synthesised and studied.[22] Silicates are chief among a limited number of substances which are prone to freeze without change of phase. If the glass so produced on solidification is reheated under suitable conditions it will devitrify, but the crystallisation apparently never results in a typical eutectic type of structure. By the reverse process of slow cooling from the molten state, however, eutectics of characteristic structure have been produced. The optical and other data obtained on these eutectics should prove helpful in future microscopical work on slagging.

The results of other mineralogical studies related to the slagging of refractories have also been published. A crystalline product of apparently unique properties was observed [23] during the microscopical examination of silica bricks which had been subjected to the action of lime/alumina/silica/iron-oxide slags. The mineral, as isolated, contained roughly 40 per cent. of $SiO_2$, 25 per cent. of CaO, 20 per cent. of $Fe_2O_3$, 8 per cent. of $Al_2O_3$ and minor proportions of other oxides; it was orthorhombic with $\alpha=1.92$, $\beta=$about 1.95 and $\gamma=2.0$. The mineral has been named " mellorite," after the late Dr. J. W. Mellor.

Mullite has been found to crystallise in various modes, depending on the temperature conditions and the crystallising medium. The types of crystallisation found in a slagged fireclay glass pot, a used fireclay zinc retort and a glazed saggar have been examined.[24] A technique for distinguishing between the $a$ and $\beta$ forms of alumina has been developed [25] from the micro-chemical method for detecting the aluminium ion by Alizarin or Alizarin-$S$. The spherulitic crystallisation of anorthite has been discussed [26] as a problem related to the action of calcareous slags on firebricks. It has previously been reported that anorthite is the chief product of reaction between blast-furnace slags and firebrick. In laboratory tests in which a cylinder of slag is placed on the surface of the brick, the anorthite invariably develops as spherulites. The factors which tend to promote the growth of spherulites of anorthite rather than normal crystals are that the area of the liquid is great compared with its depth and that the rate of cooling through the crystallisation range is fairly rapid. The concentration of anorthite in the liquid does not appear to have much effect on the formation of spherulites ; it does, however, govern their size.

The viscosity of slags and glasses has been discussed from the

standpoint of its effect on their attack on refractories.    Part 1
of this review [27] dealt with methods of measuring the viscosity of
molten silicates.    In the Margules concentric-cylinder method the
torque is measured either on the inner cylinder while the outer is
rotated or on the outer cylinder when the inner is rotated.    Rota-
tion of the inner cylinder enables viscosity measurements of from
10 to $10^7$ poise to be measured, while by rotating the outer cylinder
the apparatus is suitable for use in the range $0\cdot1$–$10^4$ poise.    Both
procedures are of use in studies on glasses and certain blast-furnace
slags, but for the more fluid open-hearth slags the second technique
should be adopted.    The measurement of the rate of fall of a sphere
through the molten mass is suitable for use with viscous glasses,
but the fall through steelworks slags is too rapid for accurate
measurement.    A modification of the concentric-cylinder method
is also useful for slags of viscosity between $0\cdot1$ and 50 poise ; in this
method the logarithmic decrement of the amplitude of oscillation of
a cylinder suspended in the molten slag is determined.    The method
is suitable for measurements on blast-furnace or open-hearth slags
at high temperatures.
    Part II of this review [28] dealt with the relationship between
viscosity, temperature and composition with particular reference
to its indication of the constitution of slags and glasses in the liquid
state.    It has been shown that molten glass may be considered an
associated liquid, the degree of association decreasing with increasing
temperature.    Recent work on the internal energy and viscosity/
composition relationships of molten soda-silica glasses suggests
compound formation in the liquid state ; viscosity/composition
isotherms in the lime-alumina-silica system also reveal discon-
tinuities at compositions corresponding to changes of phase.    The
literature on the relation between the viscosity of glasses and slags
and their attack on refractories has been summarised as Part III
of this study.[29]    It is concluded that the slagging of refractories is
a reaction between a complex liquid and a heterogeneous solid
producing a material which melts at a lower temperature than the
temperature of operation.    Such reactions are affected by the
physical properties of the attacking liquid, the refractory and the
product of reaction.    From the chemical aspect, the solubility of the
refractory in the attacking liquid is of chief importance ; theoreti-
cally, this expresses the maximum possible slagging.    Interfacial
tension, viscosity, density and size of the molecules of the slag and
product of reaction, and the physical properties of the refractory,
determine the extent to which this slagging occurs.
    The comprehensive investigation of the action of alkalies on
refractory materials has been continued since the publication of the
First Report ; the latter included a summary of Parts I to IX,
whilst Parts X and XI were reprinted in full.    Part XII has dealt [30]
with the effect of heat on refractory materials impregnated with
sodium carbonate and sodium hydroxide.    When specimens of

refractory materials are exposed to the vapour of sodium or potassium chloride at 1,000° C. uniform expansions of some magnitude have been observed. In an endeavour to simulate the uniform action of the chloride vapour with sodium hydroxide and carbonate, specimens were repeatedly impregnated with solutions of these compounds, dried and heated to 900° and 1,000° C. The length and width of the specimens were periodically measured. Silica materials expanded with the first cycle of treatment and increased in size more than the fireclay products, which did not begin to expand until an increase in weight of about 4 per cent. had occurred. The expansion is visualised as a uniform " bloating " consequent on the expulsion of gas from the interior of the brick surface, which is rendered deformable by reaction with the alkali. Experiments have also been described [31] in which the modulus of rupture at 1,000° C. was determined for fireclay, silica, siliceous and sillimanite materials exposed for different periods to the action of potassium chloride vapour, also at 1,000° C. The treatment caused a weakening of all the specimens. The fireclay materials were weakened but not appreciably softened, whereas the silica and siliceous products were markedly softened ; the sillimanite specimens were softened slightly. The difference in behaviour was attributed to the large proportion of liquid produced by reaction of the potassium chloride with the silica and siliceous products, whereas the reaction with the fireclay materials involved much less liquefaction at the same temperature. It has been demonstrated [32] that the expansion produced by the action of potassium chloride on a firebrick at 1,000° C. may be sufficient to cause cracking of the brick. In experiments on the effect of impregnations of sodium and potassium salts [33] on the transverse strength of refractories at 1,000° C., it was found that silica bricks suffered considerable reduction in strength through the fluxing action. This reduction in strength appeared to be related to the amount of soda and potash that had combined with the brick, and also to the increase in length. As a class, sodium salts caused a greater loss of strength than potassium salts. The presence of unchanged salt appeared to have little influence on the transverse strength at 1,000° C. The firebrick material treated with sodium salts was markedly softened at 1,000° C., whereas the effect of the potassium salts was rather to cause weakening through embrittlement. It was found possible to obtain some measure of correlation between these results and the indications of the relevant equilibrium diagrams.

Research on the action of gases on refractory materials has included experiments on the effect of exposure to mixtures of steam and sulphur dioxide, to chlorine, carbon monoxide and hydrocarbons. In the first part of the study [34] of the effect of steam and sulphur dioxide on refractories, a fireclay product was used as a basis for experiment at a temperature of 1,200° C. It was found that the shrinkage and reduction in porosity induced by reheating

bars for periods up to more than 200 hours were greater in steam and in sulphur dioxide than in air, oxygen, sulphur trioxide or sulphuric acid vapour, in which the shrinkages were similar.   Bars heated in steam and pure sulphur dioxide changed from a light biscuit colour to grey or brown ; after treatment, ferrous iron was present.   The extra shrinkage and colour change in steam and sulphur dioxide were attributed to the absence of free oxygen. Reheating increased the modulus of rupture in each case ;  the presence of steam aided vitrification, while sulphur trioxide nullified to some extent the effect of reheating.   This may be ascribed to the loss of bond, since in this case notable proportions of lime and magnesia were removed as sulphates on leaching with water ;  this removal of sulphates was also observed, but to a less extent, with the bars exposed to sulphur dioxide and sulphuric-acid vapour.   The quantity of sulphate formed depended on the temperature of the reaction and the atmosphere in which cooling took place, being most when it was sulphurous and least when it was inert.   A second series of experiments [35] was conducted at 600° C. On exposure to sulphuric-acid vapour or to a mixture of sulphur dioxide and oxygen, considerable increases in weight occurred, accompanied by slight contraction, marked decrease in porosity and increase in the modulus of rupture.   On extracting these test-pieces with hot dilute hydrochloric acid, appreciable quantities passed into solution, pointing to the formation of sulphates of all the bases present, but more particularly iron and aluminium sulphates.   On reheating in air at 1,000° C., the sulphates were found to decompose, the test-pieces expanding roughly to their original size.

The action of carbon monoxide on fireclay refractories received close study by the B.R.R.A. some ten years ago.  Further work is now being carried out, and, as a preliminary, a rapid method of assessing the resistance of refractory materials to disintegration by this gas has been developed.[36]   When carbon monoxide is passed over crushed firebrick contained in a fused-silica tube at 450° C., the amount of carbon dioxide produced can be used to measure the extent of the reaction $2CO=C+CO_2$, and to assess the resistance of the brick to disintegration.   The results obtained in this way on eleven brands of blast-furnace lining material, accorded well with the results obtained by the normal prolonged exposure test.   It is considered that the test may be accepted as a rapid means for evaluating blast-furnace bricks as regards this property.

In the blast furnace, the atmosphere in the stack consists of a mixture of carbon monoxide, carbon dioxide and nitrogen, with perhaps traces of other gases.   The retarding influence of the carbon dioxide on the disintegrating action of the monoxide has been examined.[37]   With mixtures containing 25 per cent. of carbon dioxide the tendency of specimens to disintegrate was found to be greatly reduced.   Carbon dioxide in concentrations of 10 per cent.

noticeably retarded the deposition of carbon round the iron spots, but when the concentration was reduced to 5 per cent. its inhibiting influence ceased.   These results have been discussed with reference to blast-furnace linings.

Experiments have been conducted [38] on the action of chlorine on fireclay and other products at 1,000° C.   Two bricks containing carbon—plumbago and silicon carbide—suffered the greatest loss, silicon tetrachloride being formed.   Magnesite and chrome bricks were also seriously attacked, but silica, sillimanite and aluminous firebricks were only slightly affected ; the reaction resulted in the formation of volatile chlorides of iron, magnesium, chromium, calcium and aluminium.   The presence of oxygen as diluent decreased but did not eliminate the attack.   The mechanism of these reactions was studied [39] by exposing pure oxides, silicates and spinels to the gas at 1,000° C.   The following was found to be the approximate decreasing order of reactivity : Iron oxide, magnesia, lime, titania, zirconia, alumina, silica.   More complex compounds containing these oxides, such as silicates and spinels, proved less reactive than the free constituent oxides.   An interesting observation was that the rate of reaction depended on the thermal history of the samples, strong precalcination reducing the chlorine attack. Experiments showed [40] that practically the whole of the iron could be removed from diatomite by treatment with chlorine.

The action of hydrocarbon gases on refractory materials is of less interest to the iron and steel industry than to the gas industry. Numerous experiments have been carried out by the B.R.R.A. on this subject during recent years.[41]

OTHER WORK OF INTEREST TO THE IRON AND STEEL INDUSTRY.

Plant work has been carried out on blast-furnace linings, an account of the first part of this work being included in the present Report.   Also of interest to the blast-furnace engineer will be an investigation recently completed on the manufacture of carbon blocks for use in blast-furnace hearths.[42]   The laboratory preparation of briquettes from foundry coke and gas-works pitch has been described, and the feasibility of dry-press or tamping methods for production on an industrial scale has been demonstrated.   The properties of the specimens prepared in the laboratory compared favourably with those of a German commercial product.

Little further work has been completed on silica refractories since the publication of the First Report.   The results of a co-operative investigation on the factors influencing the life of the silica roof of an open-hearth furnace have been published by The Iron and Steel Institute.[43]   Permanent expansion has been observed [44] when certain silica bricks have been fired to temperatures below 1,000° C.   The effect is confined to bricks rich in cristobalite

and was particularly marked in the case of a test-piece cut from the cristobalite zone of a used brick from a steel furnace roof. The growth, which occurs between 200° and 500° C., is attributed to the cristobalite inversion ; if the proportion of cristobalite present is high, the stresses produced during inversion may force the crystals apart, the physical dislocation remaining when the cristobalite reverts to the low-temperature form on cooling. Experiments showed that this low-temperature permanent expansion is but little affected by the rate of heating, but can be diminished by the application of external stress.

Continuation of the study of the properties of jointing cements has dealt with the effects of electrolyte addition to clay-grog mixtures and with the stability of certain kyanite cements. In the first investigation [45] it was demonstrated that the working properties of clay-grog mixes, as indicated by the water-retaining capacity and ability to spread under vibration, may be appreciably altered, and in some cases improved, by the addition of electrolytes. The experiments made it evident that much further work is called for on the mineralogical constitution, base-exchange properties and plastic characteristics of many types of clay. The investigation on kyanite cements was a continuation of experiments described in the First Report.[46] On calcination kyanite expands, and this later work [47] has shown that, added to sillimanite-clay cements in suitable amounts, uncalcined kyanite is beneficial in counteracting the contractile tendency of the clay bond.

High-temperature insulating refractories will probably ultimately prove economical in a number of the auxiliary furnaces on the iron and steel plant. Bricks of this type may be made from sillimanite, and experiments in the laboratory [48] have culminated in the production of high-porosity sillimanite bricks having certain useful properties.

Promising results have been obtained [49] in the preparation of refractory insulating firebricks by dry-pressing. A highly porous grog was first prepared by firing mixtures of fireclay and pulverised coal ; this grog was then graded and mixed with a further proportion of fireclay and pulverised coal, pressed and fired. This method of production has the advantage that the fired blocks are true to shape and can be fired to a high temperature without distortion. In examining the dry-press method by subjecting typical mixes in a tall mould to various pressures, it was found [50] that as the forming pressure increased, the firing shrinkage, bulk density and cold crushing strength were also increased, while the apparent porosity and permeability were decreased. It follows that in a dry-pressed insulating firebrick there will be a median layer which is less compact than the skin ; this is not serious in bricks 3 in. thick. The dry-press process has also been applied [51] to the production of an insulating firebrick with a dense, slag-resistant face. The laboratory tests which have been proposed for the evaluation of insulating

refractories have been critically reviewed [52] and have been the subject of experiment. [53]

SPECIAL PUBLICATIONS OF THE BRITISH REFRACTORIES RESEARCH ASSOCIATION.

In addition to the research investigations published in the *Bulletins* of the Association, the B.R.R.A. has issued the following three special publications during the past eighteen months :

1. Methods of Testing Basic Refractory Raw Materials and Products. (Prepared by the Testing Committee of the B.R.R.A.)
2. The Testing of Basic Refractories in the Open-Hearth Furnace. (Prepared by the Open-Hearth Refractories Joint Panel of the Iron and Steel Industrial Research Council and the B.R.R.A.)
3. Tentative Standard Methods for Testing Refractory Materials. (Prepared by the Testing Committee of the B.R.R.A.)

REFERENCES.

(NOTE.—All references are to the *Bulletin of the British Refractories Research Association* unless otherwise stated.)

1. A. A. Chadeyron and W. J. Rees, **56**, 260, 1940.
2. A. A. Chadeyron and W. J. Rees, **56**, 276, 1940.
3. A. A. Chadeyron and W. J. Rees, **54**, 8, 1940.
4. A. A. Chadeyron and W. J. Rees, **56**, 270, 1940.
5. N. E. Dobbins and W. J. Rees, **58**, 91, 1941.
6. W. Hugill and J. Vyse, **56**, 255, 1940.
7. N. E. Dobbins and W. J. Rees, **59**, 110, 118, 1941.
8. W. Hugill, A. Watts and J. Vyse, **51**, 5, 1939.
9. W. Hugill and J. Vyse, **56**, 280, 1940.
10. W. Hugill, **56**, 288, 1940.
11. T. R. Lynam, T. W. Howie and J. H. Chesters, **56**, 296, 1940.
12. A. A. Chadeyron and W. J. Rees, **59**, 106, 1941.
13. A. A. Chadeyron and W. J. Rees, **53**, 71, 1940.
14. W. Hugill and F. H. Clews, **56**, 292, 1940.
15. G. R. Rigby and A. T. Green, **58**, 63, 1941.
16. G. R. Rigby and A. T. Green, **60**, 38, 1941.
17. G. R. Rigby, W. Hugill and A. T. Green, **60**, 49, 1941.
18. W. Hugill, J. Vyse and A. T. Green, **49**, 1, 1939.
19. A. A. Chadeyron and W. J. Rees, **51**, 22, 1939.
20. W. Hugill, J. Vyse and A. T. Green, **60**, 72, 1941.
21. N. E. Dobbins, and W. J. Rees, **60**, 81, 1941.
22. W. Hugill, J. Vyse and A. T. Green, **60**, 76, 1941.
23. W. Hugill, **49**, 15, 1939.
24. G. R. Rigby, **51**, 1, 1939.
25. W. Hugill, **54**, 4, 1940.
26. W. Hugill, **53**, 69, 1940.
27. J. R. Rait, **50**, 68, 1939.
28. J. R. Rait, **50**, 114, 1939.
29. J. R. Rait and A. T. Green, **50**, 139, 1939.
30. F. H. Clews, H. M. Richardson and A. T. Green, **52**, 17, 1939.

31. F. H. Clews, H. M. Richardson and A. T. Green, **52**, 26, 1939.
32. F. H. Clews, H. M. Richardson and A. T. Green, **54,** 1, 1940.
33. F. H. Clews, H. M. Richardson and A. T. Green, **57,** 38, 1940.
34. L. R. Barrett, N. E. Dobbins and A. T. Green, **52,** 57, 1939.
35. F. H. Clews, N. E. Dobbins and A. T. Green, **57,** 20, 1940.
36. F. H. Clews, H. M. Richardson, N. E. Dobbins and G. R. Rigby, **57,** 46 1940.
37. G. R. Rigby, H. Booth and A. T. Green, **59,** 90. 1941.
38. L. R. Barrett, F. H. Clews and A. T. Green, **57,** 1, 1940.
39. H. M. Richardson, F. H. Clews and A. T. Green, **57,** 7, 1940.
40. L. R. Barrett, H. M. Richardson and A. T. Green, **57,** 19, 1940.
41. E. Rowden and A. T. Green, **38,** 68, 1935 ; **39,** 46, 53, 1936 ; E. Rowden, **44,** 10, 13, 1937 ; **48,** 50, 1938 ; **52,** 1, 1939 ; **57,** 30, 1940.
42. G. R. Rigby, H. Booth and A. T. Green, **59,** 77, 1941.
43. Open-Hearth Refractories Joint Panel, *Journal of the Iron and Steel Institute*, 1941, No. II., p. 203 P.
44. G. R. Rigby, A. E. Dodd, R. P. White and A. T. Green, **59,** 99, 1941.
45. F. H. Clews, H. M. Richardson and A. T. Green, **52,** 31, 1939.
46. F. H. Clews and A. T. Green, First Report on Refractory Materials, *Iron and Steel Institute*, 1939, *Special Report No.* 26, p. 401.
47. F. H. Clews, H. M. Richardson and A. T. Green, **52,** 38, 1939.
48. F. H. Clews, N. E. Dobbins and A. T. Green, **52,** 42, 1939.
49. L. R. Barrett, J. F. Clements and A. T. Green, **57,** 57, 1940.
50. L. R. Barrett, W. F. Ford and A. T. Green, **57,** 86, 1940.
51. L. R. Barrett, J. F. Clements and A. T. Green, **57,** 71, 1940.
52. L. R. Barrett, F. H. Clews and A. T. Green, **55,** 67, 1940.
53. L. R. Barrett, W. F. Ford and A. T. Green, **57,** 95, 1940.